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16. ABSTRACT The Environmental Monitoring and Support Laboratory-Cincinnati of EPA conducts EPA's quality assurance program for the water laboratories and assists EPA laboratories in the choice of methods for physical, chemical, biological and microbiological analyses. The responsibility for quality assurance activities of EMSL is assigned to the Quality Assurance Branch (QAB). This study, one of the QAB activities, describes a joint EPA/ASTM evaluation study of a method of analysis for total mercury in natural water and wastewaters. The method includes an acid-permanganate-persulfate digestion followed by reduction and measurement of mercury in the vapor phase at 253.7 nm. This report describes the study, its conclusions and provides statements of precision and accuracy.			
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EPA METHOD STUDY 8,
TOTAL MERCURY IN WATER

by

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Prepared in part under EPA Purchase Order 5-03-4294

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DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory-Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate technique to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid wastes.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microorganisms in water. Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This publication of the Environmental Monitoring and Support Laboratory, Cincinnati, entitled: EPA Method Study 8, Total Mercury in Water reports the results of a joint ASTM/EPA study of a cold vapor technique for total mercury in water, prior to acceptance by both organizations. Federal agencies, states, municipalities, universities, private laboratories, and industry should find this evaluative study of a selected method of analysis for mercury of vital importance in their efforts in monitoring and controlling mercury pollution in the environment.

Dwight G. Ballinger
Director, EMSL - Cincinnati

ABSTRACT

The Office of Research and Development, EPA, coordinates the collection of water quality data to determine compliance with water quality standards, to provide information for planning of water resources development, to determine the effectiveness of pollution abatement procedures, and to assist in research activities. In a large measure the success of the pollution control program rests upon the reliability of the information provided by the data collection activities.

The Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati, Ohio, is responsible for insuring the reliability of physical, chemical, biological, and microbiological data generated in the water programs of EPA. Within EMSL, the Quality Assurance Branch (QAB) conducts interlaboratory studies for method evaluation and laboratory accreditation programs, provides quality control samples, and develops quality control guidelines for water quality laboratories.

This report describes one study in the series conducted by the Quality Assurance Branch. It was completed in part by Mr. Robert C. Kroner under EPA Purchase Order 5-03-4294.

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INTRODUCTION

The various analytical laboratories of the U.S. Environmental Protection Agency gather water quality data to provide information on water resources, to assist research activities, and to evaluate pollution abatement activities. The success of these pollution control activities depends upon the reliability of the data provided by the laboratories, particularly when legal action is involved.

The Environmental Monitoring and Support Laboratory-Cincinnati (EMSL, formerly Methods Development and Quality Assurance Research Laboratory) of EPA was established to conduct EPA's quality assurance program for the water laboratories and to assist EPA laboratories in the choice of methods for physical, chemical, biological and microbiological analyses. The quality assurance program of EMSL is designed to maximize the reliability and legal defensibility of all water quality information collected by EPA laboratories. The responsibility for these activities of EMSL is assigned to the Quality Assurance Branch (QAB). This study is one of the QAB activities.

Prior to this method evaluation study, the research chemists of EMSL, assisted by other chemists in EPA, had proposed a method of measurement for total mercury in natural water and wastewaters. The method developed after considerable study included an acid-permanganate-persulfate digestion at 95°C for two hours followed by reduction and measurement of mercury in the vapor phase at 253.7 nm.

Since EPA chemists are participating members of the D-19 Committee on Water of the American Society for Testing and Materials, the same method was proposed to the D-19 Committee for use in the Annual Book of ASTM Standards, Part 31, Water. It was logical therefore to propose a joint EPA/ASTM study for mercury in water. This report describes the study and provides statements of precision and accuracy for the method.

SUMMARY

The Quality Assurance Branch of the Environmental Monitoring and Support Laboratory conducted a joint EPA/ASTM interlaboratory study on the cold vapor technique for mercury in natural waters.

The method evaluated in this study is that described by Kopp, Longbottom, and Lobring (1) which requires a vigorous digestion with acid permanganate, potassium persulfate and heat (95°C) to effect complete oxidation of organically bound mercury prior to reduction and measurement by absorption at 253.7 nm.

Sample concentrates were prepared at similar, but slightly different, concentrations of mercury. An aliquot of each concentrate was added to distilled water and natural water samples at concentrations of 0.2-10 µg of mercury/liter. One mercury measurement was made on the natural water as background and one measurement each on the distilled water and natural water samples with the added increment. Recoveries from the natural water samples were calculated by difference. Recoveries for all concentrations were compared and significant statistical measures such as standard deviation, mean recovery, etc., were calculated. The following equations provide the precision and accuracy which may be expected in routine work:

Distilled Water:

$$\text{Precision } S = 0.2454 + 0.2922 \bar{X}$$

$$S_r = 0.3117 + 0.0718 \bar{X}$$

Accuracy

$$\text{Mean Recovery, } \bar{X} = 0.2028 + 0.9517 (\text{conc})$$

Natural Water:

$$\text{Precision } S = 0.1661 + 0.3647 \bar{X}$$

$$S_r = 0.0465 + 0.1379 \bar{X}$$

Accuracy

$$\text{Mean Recovery, } \bar{X} = 0.1373 + 0.9508 (\text{conc})$$

DESCRIPTION OF STUDY

The study design was based on Youden's original plan (2) for collaborative evaluation of precision and accuracy for analytical methods. According to Youden's design, samples are analyzed in pairs, and each sample of a pair has a slightly different concentration of the constituent. The analyst is directed to do a single analysis and report one value for each sample, as if for a normal routine sample.

In this study, samples were prepared as concentrates in sealed glass ampuls and presented to the analyst with complete instructions. The analyst was required to add an aliquot of each concentrate to a volume of distilled water and to a volume of natural water of any kind. Analysis in distilled water evaluates the proficiency of the analyst to use the method on a sample free of interferences; analysis in natural water (rivers, lakes, estuaries) is intended to reveal interferences in the method. Four pairs of samples were used. One pair contained mercury near the minimum detectable limit of 0.2 $\mu\text{g/liter}$; a second pair contained mercury at an intermediate level of 0.5-0.6 $\mu\text{g/liter}$ level and the latter pairs contained mercury at levels of 3-10 $\mu\text{g/liter}$.

Test Design

A summary of the test design, using Youden's non-replicate technique for x and y samples is given below:

- 1) Eight samples, prepared as stable concentrates in sealed glass ampuls, were presented to the analyst as unknowns.
- 2) When the analyst was ready to start the analysis, the ampuls were opened and an aliquot diluted to volume in distilled water and in a natural water according to instructions.
- 3) Four levels of mercury concentration (four pairs of samples) were analyzed to cover the levels observed in natural waters.
- 4) Each sample was analyzed once only.
- 5) Natural water samples were analyzed with and without added increment and the added level determined by difference.

Recoveries from distilled water and natural waters were compared. Precision and accuracy were calculated and interferences were observed.

Preparation of Samples

Sample concentrates were prepared by dissolving precisely-weighed amounts of reagent grade chemicals in high purity water* to produce accurate concentrations of organic and inorganic mercury. Each sample contained the same ratio of inorganic to organic mercury (42%:58%) as mercuric chloride and methyl mercury chloride, respectively. The concentrates were preserved with 0.15% redistilled nitric acid and checked by repeated analysis for a period of three months prior to distribution. These analyses served to confirm both the calculated concentrations and sample stability. Analyses of the samples by an outside laboratory also confirmed the concentrations.

When diluted to volume according to the instructions, the samples contained the following concentrations of mercury:

TABLE 1
True Values for Total Mercury**

Sample	Concentration of Mercury µg/liter
1	0.21
2	0.27
3	0.51
4	0.60
5	3.4
6	4.1
7	8.8
8	9.6

* Prepared by passage of distilled water through a four-cartridge Millipore Super-Q system.

** The concentrations are the actual levels calculated and added. They are not based on analysis, the latter being used for verification only.

Analysis and Reporting

The distilled water - natural water spike technique was used in this study. Each analyst was instructed to dilute separate 5.0 ml aliquots of each concentrate to one liter with distilled water and a natural or wastewater of his choice. To insure sample stability the analyst was also instructed to add 1.5 ml of redistilled nitric acid per liter during sample preparation. Accurate measurement of mercury in distilled water confirmed the analyst's ability to measure mercury in a sample free of interferences. A difference in the recovery of mercury from distilled water as compared to the recovery of mercury from natural water indicated the presence of interferences.

Distribution of Samples

An invitational memorandum announced the study to each EPA Region in September, 1972. The study was also announced in EPA's *Analytical Quality Control Newsletter* which is circulated to about 7,000 technical offices of government and private agencies in the United States and Canada.

One-hundred and one laboratories from EPA, other Federal, State and local agencies, Canadian groups, universities and private industry responded and participated. After a pre-selected cutoff date, beyond which no further requests were answered, samples were packed and shipped.

Each collaborator was sent 1) a set of eight ampuls, 2) instructions for sample preparation, 3) a copy of the analytical procedure to be used, and 4) duplicate report sheets. Participants were allowed fifty days to complete the analyses and report the data. All data returned within the prescribed time were included in this report; data reported later than the cutoff date were omitted.

RESULTS

Tables 2 and 3 present all raw data received, identified by laboratory and analyst codes.

TABLE 2

Raw Data from Analyses for Total Mercury Increment
in Distilled Water

		AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6	AMPUL 7	AMPUL 8
INCREMENT, UG/L		0.21	0.27	0.51	0.60	3.4	4.1	8.8	9.6
LAB NO.	ANALYST NO.								
101	1	0.10	0.23	0.50	0.64	3.80	4.30	8.35	9.60
105	1	0.40		0.60	0.60	3.80	4.50	9.30	9.60
106	1	0.50	0.50	0.50	0.50	3.50	4.50	10.00	11.00
110	1	0.07	0.21	0.35	0.60	2.00	2.50	8.00	6.20
112	1	0.61	0.34	0.52	0.51	3.10	4.30	8.70	9.70
117	1	0.37	0.31	0.56	0.81				
122	1	0.21	0.31	0.46	0.57	3.20	4.20	8.70	9.00
123	1	0.20	0.20	0.40	0.40	4.20	4.80	9.40	10.00
124	1	0.50	0.36	0.58	0.83	4.40	5.10	9.60	11.00
125	1	1.00	1.00	1.00	1.00	1.48	1.25	3.30	4.25
137	1	0.10	0.10	0.10	0.22	1.60	4.40	4.40	4.80
142	1	0.22	0.27	0.50	0.56	3.10	3.50	7.80	8.30
145	1	0.40	0.30	0.50	0.80	3.20	3.50	9.00	9.20
148	1	0.40	0.65	0.75	0.81	3.30	3.80	8.00	7.60
152	1	0.43	0.29	0.53	0.67	3.60	4.10	9.30	9.90
157	1	0.38	0.35	0.58	0.60	3.40	4.20	8.50	9.30
169	1	0.10	0.20	0.30	0.50	3.70	4.20	8.20	8.90
180	1	0.20	0.30	0.50	0.60	3.14	4.27	10.00	13.30
180	2	0.21	0.32	0.55	0.64	3.43	4.70	10.00	13.25
180	3	0.24	0.44	0.53	0.70	3.50	4.40	5.00	10.00
182	1	0.15	0.17	0.38	0.53	3.50	4.30	9.10	10.00
184	1	0.20	0.20	0.38	0.61	3.10	3.70	8.20	9.00
185	1	0.23	0.29	0.52	0.49	3.10	3.73	7.43	7.89
190	1	0.20	0.20	0.40	0.55	3.20	4.10	8.50	8.90
195	1	0.30	0.30	1.10		6.30	7.70	13.20	13.50
204	1	0.58	0.20	0.42	0.60	3.80	4.38	6.80	8.48
212	1	0.11	0.21	0.35	0.45	3.40	4.20	8.60	9.10
230	1	0.22	0.27	0.52	0.60	3.30	4.10	9.00	9.20
233	1	0.80	0.80	1.00	1.00	4.70	5.60	10.60	10.80
233	2	0.48	0.49	1.05	0.95	4.85	4.95	10.05	9.95
253	1	0.20	0.30	0.60	0.20	4.40	6.00	11.00	10.00
259	1	0.20	0.20	0.45	0.56	3.10	3.60	7.40	8.10
261	1	0.40	0.40	1.00	15.40R	3.20	3.80	9.40	8.40
262	1	0.50	0.20	0.40	0.20	3.30	4.00	8.40	9.10
267	1	0.43	0.60	0.68	0.64	2.10	2.60	4.20	4.60
311	1	0.80	1.00	7.80R	8.90R	120.00R	148.00R	328.00R	382.00R
324	1	1.60	10.60R	5.40R	1.60	3.20	3.40	8.00	9.10
329	1	3.00R	1.44	6.28R	1.28	2.28	5.56	4.56	10.40
352	1	0.50	0.50	2.30	2.30	4.00	4.20	7.50	7.70
356	1	0.20	0.30	0.50	0.50	1.20	0.90	2.00	2.30
374	1	1.00	0.95	1.53	1.29	4.91	5.86	10.99	11.85
422	1	0.46	0.50	0.98	0.94	4.87	5.89	11.88	12.80
436	1	0.40	0.40	0.50	0.70	3.50	4.50	9.50	10.00
437	1	0.50	0.35	0.32	0.52	2.45	3.10	7.50	7.30
441	1	0.14	0.16	0.25	0.26	1.40	1.65	3.35	3.59
442	1	0.35	0.35	0.45	0.60	3.20	4.00	9.00	9.80
443	1	0.44	0.44	0.56	0.57	3.50	4.30	9.00	9.50
446	1	0.40	0.50	0.70	0.80	3.90	4.30	9.30	9.80
447	1	0.11	0.19	0.38	0.45	2.40	4.10	7.90	7.20
448	1	0.20	0.36	0.27	0.45	1.50	2.10		4.80
452	1		0.40	0.50	0.50	2.80	3.40	7.30	7.50
457	1	0.90	0.90	3.80R	4.00R	28.00R	30.00R	63.00R	68.00R
467	1	0.29	0.26	1.74	6.46R	2.75	3.21	6.85	8.80
468	1	0.55	1.70	0.48	0.75	3.20	3.80	8.30	9.00
471	1	0.30	0.20	0.30	0.50	2.00	2.90	6.20	8.80

R = REJECTED

TABLE 2
(Continued)

Raw Data from Analyses for Total Mercury Increment
in Distilled Water

LAB NO.	ANALYST NO.	INCREMENT, UG/L							
		AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6	AMPUL 7	AMPUL 8
		0.21	0.27	0.51	0.60	3.4	4.1	8.8	9.6
472	1	0.05	0.71	1.37	0.34	0.67	1.11	3.14	1.18
475	1	0.20	0.30	0.50	0.50	3.50	4.40	8.80	10.00
478	1	0.80	0.80	1.20	0.60	4.20	4.60	9.40	10.40
481	1	0.50	0.45	0.82	0.92	3.08	5.08	10.75	11.03
486	1	0.32	0.38	0.52	0.62	3.50	4.20	9.00	9.90
489	1	0.20	0.17	0.34	0.51	4.00	5.90	13.00	13.00
492	1	0.60	0.58	1.10	1.14	3.10	3.70	6.00	9.60
496	1	0.28	0.32	0.58	0.70	3.50	4.10	8.30	9.00
500	1	0.83	0.63	1.20	1.20	4.20	5.40	12.00	14.00
502	1			0.63	1.20				
503	1	1.00	0.90	1.00	0.95	3.45	3.90	7.00	9.10
504	1	0.15	0.15	0.40	0.70	3.36	4.22	8.56	8.34
508	1	0.52	0.40	1.80	1.20	4.10	4.60	11.60	12.50
509	1	0.60	0.70	0.60	1.80	3.10	3.80	7.70	7.80
510	1	0.35	0.25	0.65	0.55	3.40			
511	1	0.75	0.80	0.90	1.00	3.00	3.80	8.10	8.20
512	1	0.23	0.28	0.54	0.65	3.50	4.10	8.70	9.30
513	1	0.50		0.48	0.52	3.50	4.10	9.00	9.00
514	1	0.43	0.79	0.28	0.20	3.20	3.90	9.30	9.60
515	1	0.38	0.30	0.58	0.64	3.30	4.10	9.10	9.60
516	1	0.20	0.20	0.20	0.40	3.30	4.60	10.00	12.00
517	1	1.00	0.91	0.36	0.18	2.00	3.60	6.30	7.50
518	1	0.20	0.20	0.40	0.50	3.00	4.90	8.60	11.20
519	1	1.00	1.00	1.00	1.00	4.00	5.00	9.00	10.00
520	1	0.37	0.25			3.80	4.50	11.00	13.00
521	1	0.41	0.41	0.65	0.98	3.50	4.60	8.40	8.80
522	1	0.41	0.16	0.61	0.69	3.81	4.29	10.51	11.96
523	1	0.2R	0.30	0.50	0.60	3.50	4.20	9.10	10.00
524	1	0.6	0.80	1.10	0.80	3.60	4.50	10.20	11.40
525	1	0.45	0.50	1.10	1.10	4.70	5.20	9.20	9.70
526	1	0.20	0.30	0.35	0.35	3.80	4.00	8.00	8.20
527	1		0.26	0.41	0.52	2.60	3.30	7.20	8.00
528	1	0.40	0.40	1.20	0.30	3.20	7.50	3.60	4.10
529	1	1.00	0.50	1.00	2.50	6.25	8.00	12.00	15.75
530	1		0.20	0.45	0.35	1.90	10.60		5.20
531	1	0.00	1.64	3.92R	1.39	23.10R	5.40	36.40R	18.60
532	1	3.75R	5.00R	7.00R	7.00R	11.30	16.30R	20.00	25.00
533	1	12.10R	14.30R	0.65	0.88	3.30	6.70	9.80	9.30
534	1	0.23	0.04	0.04	0.03	0.20	0.20	0.55	0.58
535	1	4.10R	4.80R	5.70R	3.00	4.80	3.30	10.00	10.00

R = REJECTED

TABLE 3

Raw Data from Analyses for Total Mercury Increment
in Natural Water

LAB NO.	ANALYST NO.	INCREMENT, UG/L							
		AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6	AMPUL 7	AMPUL 8
		0.21	0.27	0.51	0.60	3.4	4.1	8.8	9.8
101	1	0.15	0.30	0.64	0.69	3.60	4.30	8.43	9.40
105	1	0.20		0.60	0.80	4.00	5.00	8.00	9.10
106	1	0.50	0.50	0.50	0.50	3.50	4.00	9.50	10.50
110	1	0.07	0.21	0.35	1.00	2.10	2.50	6.10	6.20
112	1	0.30	0.35	0.42	0.46	3.30	4.40	8.40	9.20
117	1					4.80	5.00	10.30	12.80
122	1	0.10	0.26	1.06	0.38	3.60	4.00	8.20	8.70
123	1		0.20	0.20	0.60	4.40	4.70	9.70	9.70
124	1	0.30	0.27	0.57	0.75	4.20	4.80	9.80	11.00
125	1	1.00	1.00	1.00	1.00	0.85	0.83	1.88	1.98
137	1	0.10	0.11	0.11	0.22	1.80	2.30	4.50	5.00
142	1	0.22	0.27	0.50	0.58	3.30	3.70	7.80	8.30
145	1	0.40		0.50		3.00		8.30	
148	1	0.30	0.15	0.22	0.50	2.80	3.70	10.40	8.30
152	1	0.29	0.30	0.55	0.80	3.40	4.10	8.80	9.60
157	1	0.35	0.35	0.40	0.60	3.50	4.20	8.50	9.50
169	1	0.10	0.20	0.40	0.50	3.60	4.00	8.10	9.00
184	1	0.20	0.23	0.46	0.61	3.20	3.90	8.70	9.20
185	1	0.23	0.31	0.51	0.64	2.94	3.77	7.54	7.80
190	1	0.22	0.26	0.47	0.53	3.30	4.20	8.40	8.80
204	1	0.20	0.20	0.37	0.49	2.79	2.79	6.36	6.72
212	1	0.32	0.16	0.35	0.72	3.60	4.69	9.10	9.50
230	1	0.14	0.19	0.40	0.45	2.90	3.50	10.70	
233	1	0.80	0.80	1.00	1.00	4.70	5.69	10.60	10.80
233	2	0.48	0.49	1.05	0.95	4.85	4.95	10.05	9.95
253	1	0.20	0.20	0.70	0.20	5.40	5.09	12.00	10.00
259	1	0.20	0.21	0.45	0.58	3.10	3.60	7.40	8.10
261	1	0.00	0.80	0.20	10.00R	3.00	3.20	8.40	7.80
262	1	0.30	0.20	0.40	0.60	3.70	4.50	9.00	10.00
267	1	0.44	0.61	0.69	0.66	2.60	2.70	3.90	4.00
311	1	0.80	1.00	8.00R	8.70R	125.00R	155.00R	340.00R	379.00R
324	1	2.20R	7.50R	4.20R	1.60	1.70	3.90	8.00	8.50
329	1	0.39	0.10	0.10	0.10	0.13	0.77	2.45	3.55
352	1	0.64	0.59	2.40	2.30	4.20	4.20	7.80	8.00
356	1	0.10	0.50	0.40	0.80	3.70	1.70	3.00	4.10
374	1	1.27	1.05	1.46	1.32	5.06			
422	1	0.27	0.40	0.62	0.91	4.84	5.82	11.98	13.27
436	1	0.50	0.50	0.50	0.50				
441	1	0.13	0.15	0.26	0.25	1.36	1.70	3.42	3.52
442	1	0.40	0.42	0.62	0.60	3.40	4.00	9.40	10.00
443	1	0.56	0.32	0.66	0.49	3.80	3.90	8.50	9.50
446	1	0.40	0.50	0.70	1.00	3.50	4.30	9.00	12.00
447	1	0.26	0.24	0.34	0.62	2.40	3.09	6.60	6.20
448	1	0.50	0.20	0.80		2.10	3.09		3.80
452	1		0.40	0.50	0.50	2.80	3.49	7.30	7.50
457	1	0.90	1.10	4.00	3.90R	30.00R	33.00R	66.00R	72.00R
468	1	0.49	1.00	0.28	0.35	3.50	4.00	8.30	9.40
471	1	0.20	0.10	0.20	0.30	2.10	3.19	6.30	9.00
472	1	0.08	0.65	1.44	0.44	0.64	1.10	3.22	1.18
475	1	0.20	0.20	0.30	0.40	2.10	2.20	4.80	5.10
478	1	1.20	0.80	1.20	1.20	3.80	4.40	9.00	10.00
481	1	0.48	0.53	0.93	0.96	3.48	4.58	11.03	11.98
486	1	0.30	0.35	0.52	0.60	3.50	4.30	8.60	9.80
489	1	0.10	0.16	0.35	0.46	4.00	5.69	13.00	14.00
492	1	0.44	0.46	1.10	0.90	3.20	4.09	8.30	9.00

R = REJECTED

TABLE 3
(Continued)

Raw Data from Analyses for Total Mercury Increment
in Natural Water

		AMPUL 1	AMPUL 2	AMPUL 3	AMPUL 4	AMPUL 5	AMPUL 6	AMPUL 7	AMPUL 8
INCREMENT, UG/L		0.21	0.27	0.51	0.60	3.4	4.1	8.8	9.6
LAB NO.	ANALYST NO.								
496	1	0.30	0.31	0.60	0.72	3.70	4.10	8.50	9.20
500	1	0.22	0.00	0.40	0.40	3.00	4.10	12.00	17.00
503	1	0.25	0.65	1.10	1.05	3.95	4.25	9.45	9.05
504	1	0.15	0.80	0.60	0.70	3.41	4.22	7.76	8.34
508	1	0.47	0.35	0.95	1.50	3.80	4.30	11.20	11.80
510	1	0.00	0.25	0.40		3.15	3.73	8.10	
511	1	0.80	1.20	1.40	1.50	3.55	4.50	8.35	10.70
512	1	0.24	0.28	0.56	0.65	3.50	4.00	8.50	9.10
514	1	0.40	0.40	0.50	0.50	2.80	4.00	8.90	9.60
515	1	0.30	0.33	0.56	0.64	3.30	4.10	9.10	9.60
516	1	0.22	0.44	0.77	0.73	4.20	4.50	11.00	11.00
517	1	0.00	0.78	0.40	0.16	2.10	3.10	6.57	7.60
518	1	0.20	0.40	0.40	0.50	3.40	4.00	8.60	11.80
519	1	1.00	1.00	1.00	1.00	4.00	4.00	9.00	9.00
520	1	0.18	0.32	0.65	1.10	3.80	4.50	11.00	12.00
521	1	0.03	0.00	0.20	0.40	3.80	4.80	8.20	8.90
522	1	0.16	0.06	0.32	0.35	2.96	3.46	7.21	7.96
523	1	0.20	0.25	0.50	0.60	3.40	4.10	8.90	9.80
524	1		1.00	1.40	1.20	3.00	4.30	13.80	10.70
525	1	0.45	0.50	1.10	1.30	4.60	5.20	9.00	9.80
526	1	0.20	0.30	0.40	0.50	2.50	3.20	6.80	7.30
527	1		0.24	0.44	0.55	2.80	3.30	7.50	8.10
529	1	1.00	0.50	0.75	1.00	5.00	6.50	15.75	14.50
530	1		0.30	0.30	0.30	7.20	21.00R		5.40
531	1	3.35R	2.09R	18.48R	2.66R	18.86R	19.00R	28.00	15.40
532	1	4.75R	5.75R	7.50R	7.50R	12.50		21.30	26.30
533	1	1.80R	2.60R	1.70	1.70	2.90	2.40	13.00	12.60
534	1	0.00	0.07	0.01	0.00	0.16	0.17	0.53	0.34
535	1	4.70R	3.80R	4.30R	4.20R	3.50	3.90	7.20	7.20

R = REJECTED

TREATMENT OF DATA

Rejection of Outliers

This study, done at low and fractional $\mu\text{g/liter}$ levels, produced some data which were orders of magnitude away from the true values. These extraneous values had to be eliminated before beginning any data evaluations. If these were not removed, the deviations in the data would indicate a misleadingly large standard deviation for the method. To prevent this from happening, those values which were further than four standard deviations from the mean, as calculated from all data, were discarded as outliers. Assuming a normal distribution, there is a 99.994% probability that the rejected data were properly discarded.

After elimination of unreasonable data, it was necessary to remove the remaining extreme values which had only a small chance of validity and which would make a significant change in the precision and accuracy values for the tested levels of mercury. These abnormal values are a part of the routine data in every interlaboratory study, resulting from chemical, instrumental, and analyst error. These outliers were rejected by applying the two-tailed Student's t test to all values at a 99% probability level. This gave a 99 to 1 assurance that the data rejected were indeed true outliers and should be discarded.

As the spread of valid data increases, fewer outliers are rejected because of a large standard deviation in the denominator of the t test. Similarly, when the spread of valid data is very small the t test is more powerful and more of the outliers are detectable. In either case, the rejected values should be considered true outliers and the analytical conditions should be carefully reviewed for the cause of error.

Basic Data Summaries

Complete data summaries are given in Tables 4 through 19. Each Table provides a statistical evaluation of the data for a single concentrate spiked into one type of water. With the exception of "N, ALL DATA" and "MEAN, ALL", the statistical parameters are based on the data remaining after the rejection of outliers (retained data).

In addition to the statistical measurements, all data are ranked in ascending order and retained data are presented in a histogram using $\sqrt{n}$ cell divisions. Each X in the histogram represents one analytical result for 1-15 values/cell. When more than 15 values occur per cell, only 15 X's are printed but the actual number of values included in the cell is printed to the left.

TABLE 4

Data Summary by Ampul, Analyses for
Total Mercury in Distilled Water

AMPUL 1 INCREMENT = 0.21 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	91	RANGE	1.60000	COEF. VAR.	0.66864
TRUE VAL.	0.21	VARIANCE	0.07800	SKWNESS	1.38637
MEAN, ALL	0.65154	STD. DEV.	0.27929	NO. OF CELLS	9
MEAN, RET.	0.41770	CONF. LIM.	±0.55367 (95 PCT)		
MEDIAN	0.38000				
ACCURACY	98.90502	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER

MIDPOINT FREQ. HISTOGRAM
RETAINED DATA ONLY

0.00	0.30	0.60	0.0889	11	XXXXXXXXXX
0.05	0.30	0.60	0.2667	29	XXXXXXXXXXXXXX
0.07	0.32	0.61	0.4444	28	XXXXXXXXXXXXXX
0.10	0.35	0.75	0.6222	5	XXXXX
0.10	0.35	0.80	0.8000	6	XXXXXX
0.10	0.37	0.80	0.9778	7	XXXXXXX
0.11	0.37	0.80	1.1556	0	
0.11	0.38	0.80	1.3333	0	
0.14	0.38	0.83	1.5111	1	X
0.15	0.40	0.90			
0.15	0.40	1.00			
0.20	0.40	1.00			
0.20	0.40	1.00			
0.20	0.40	1.00			
0.20	0.40	1.00			
0.20	0.40	1.00			
0.20	0.41	1.60			
0.20	0.41	3.00R			
0.20	0.43	3.75R			
0.20	0.43	4.10R			
0.20	0.43	17.10R			
0.20	0.44				
0.20	0.45				
0.20	0.46				
0.20	0.48				
0.21	0.50				
0.21	0.50				
0.22	0.50				
0.22	0.50				
0.23	0.50				
0.23	0.50				
0.23	0.50				
0.24	0.52				
0.28	0.55				
0.29	0.58				

R = REJECTED DATA

TABLE 5

Data Summary by Ampul, Analyses for
Total Mercury in Distilled Water

AMPUL 2 INCREMENT = 0.27 US/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	92	RANGE	1.79999	COEF. VAR.	0.72238
TRUE VAL.	0.27	VARIANCE	0.10551	SKEWNESS	2.02945
MEAN, ALL	0.80728	STD. DEV.	0.32482	NO. OF CELLS	9
MEAN, RET.	0.44965	CONF. LIM.	±0.64026 (95 PCT)		
MEDIAN	0.33000				
ACCURACY	66.54010	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.04	0.30	0.65	0.1400	22	XXXXXXXXXXXXXXXXXX
0.10	0.30	0.70	0.3400	35	XXXXXXXXXXXXXXXXXX
0.15	0.30	0.71	0.5400	13	XXXXXXXXXXXXXXXXXX
0.16	0.30	0.79	0.7400	8	XXXXXXXXXX
0.16	0.30	0.80	0.9400	7	XXXXXXX
0.17	0.31	0.80	1.1400	0	
0.17	0.31	0.80	1.3400	0	
0.19	0.32	0.80	1.5400	1	X
0.20	0.32	0.90	1.7400	2	XX
0.20	0.34	0.90			
0.20	0.35	0.91			
0.20	0.35	0.95			
0.20	0.35	1.00			
0.20	0.36	1.00			
0.20	0.36	1.00			
0.20	0.36	1.44			
0.20	0.40	1.70			
0.20	0.40	1.84			
0.20	0.40	4.80R			
0.21	0.40	5.00R			
0.21	0.40	10.60R			
0.23	0.41	14.30R			
0.25	0.44				
0.25	0.44				
0.26	0.45				
0.26	0.49				
0.27	0.50				
0.27	0.50				
0.28	0.50				
0.29	0.50				
0.29	0.50				
0.30	0.50				
0.30	0.58				
0.30	0.60				
0.30	0.63				

R = REJECTED DATA

TABLE 6

Data Summary by Ampul, Analyses for
Total Mercury in Distilled Water

AMPUL 3 INCREMENT = 0.51 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	94	RANGE	2.25999	COEF. VAR.	0.57526
TRUE VAL.	0.51	VARIANCE	0.14130	SKEWNESS	1.70852
MEAN, ALL	1.02929	STD. DEV.	0.37590	NO. OF CELLS	9
MEAN, RET.	0.65244	CONF. LIM.	±0.74937 (95 PCT)		
MEDIAN	0.52000				
ACCURACY	28.12685	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.04	0.50	1.00	0.1656	6	XXXXXX
0.10	0.50	1.00	0.4167	41	XXXXXXXXXXXXXXXXXX
0.20	0.50	1.00	0.6678	18	XXXXXXXXXXXXXXXXXX
0.25	0.50	1.00	0.9189	9	XXXXXXXXXX
0.27	0.50	1.05	1.1700	8	XXXXXXX
0.28	0.52	1.10	1.4211	2	XX
0.30	0.52	1.10	1.6722	1	X
0.30	0.52	1.10	1.9233	1	X
0.32	0.52	1.10	2.1744	1	X
0.34	0.53	1.20			
0.35	0.53	1.20			
0.35	0.54	1.20			
0.35	0.55	1.37			
0.36	0.56	1.53			
0.38	0.56	1.74			
0.38	0.58	1.80			
0.38	0.58	2.30			
0.40	0.58	3.80R			
0.40	0.58	3.92R			
0.40	0.60	5.40R			
0.40	0.60	5.70R			
0.40	0.60	6.28R			
0.41	0.61	7.00R			
0.42	0.65	7.80R			
0.45	0.65				
0.45	0.65				
0.45	0.65				
0.46	0.68				
0.48	0.70				
0.48	0.75				
0.50	0.82				
0.50	0.90				
0.50	0.98				
0.50	1.00				
0.50	1.00				

R = REJECTED DATA

TABLE 7

Data Summary by Ampul, Analyses for
Total Mercury in Distilled Water

AMPUL 4 INCREMENT = 0.60 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	93	RANGE	2.97000	COEF. VAR.	0.62637
TRUE VAL.	0.60	VARIANCE	0.21709	SKEWNESS	2.34514
MEAN, ALL	1.15289	STD. DEV.	0.46593	NO. OF CELLS	9
MEAN, RET.	0.74386	CONF. LIM.	±0.92354 (95 PCT)		
MEDIAN	0.60000				
ACCURACY	23.97704	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.03	0.57	0.98	0.1950	11	XXXXXXXXXXXX
0.18	0.60	1.00	0.5250	42	XXXXXXXXXXXXXXXXXXXX
0.20	0.60	1.00	0.8550	22	XXXXXXXXXXXXXXXXXXXX
0.20	0.60	1.00	1.1850	7	XXXXXXX
0.20	0.60	1.00	1.5150	2	XX
0.22	0.60	1.10	1.8450	1	X
0.26	0.60	1.14	2.1750	1	X
0.30	0.60	1.20	2.5050	1	X
0.34	0.60	1.20	2.8350	1	X
0.35	0.60	1.20			
0.35	0.61	1.28			
0.40	0.62	1.29			
0.40	0.64	1.39			
0.45	0.64	1.60			
0.45	0.64	1.80			
0.45	0.64	2.30			
0.49	0.65	2.50			
0.50	0.67	3.00			
0.50	0.69	4.00R			
0.50	0.70	6.46R			
0.50	0.70	7.00R			
0.50	0.70	8.90R			
0.50	0.70	15.40R			
0.50	0.75				
0.51	0.80				
0.51	0.80				
0.52	0.80				
0.52	0.81				
0.52	0.81				
0.53	0.83				
0.55	0.88				
0.55	0.92				
0.56	0.94				
0.56	0.95				
0.57	0.95				

R = REJECTED DATA

TABLE 8

**Data Summary by Ampul, Analyses for
Total Mercury in Distilled Water**

AMPUL 5 INCREMENT = 3.4 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	93	RANGE	11.10000	COEF. VAR.	0.37856
TRUE VAL.	3.40	VARIANCE	1.65755	SKEWNESS	2.31488
MEAN, ALL	5.13096	STD. DEV.	1.28746	NO. OF CELLS	9
MEAN, RET.	3.40088	CONF. LIM.	± 2.53740 (95 PCT)		
MEDIAN	3.38000				
ACCURACY	0.02595	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.20	3.20	3.81	0.8167	4	XXXX
0.67	3.20	3.90	2.0500	12	XXXXXXXXXXXX
1.20	3.20	4.00	3.2833	55	XXXXXXXXXXXX
1.40	3.30	4.00	4.5167	16	XXXXXXXXXXXX
1.48	3.30	4.00	5.7500	2	XX
1.50	3.30	4.10	6.9833	0	
1.60	3.30	4.20	8.2167	0	
1.90	3.30	4.20	9.4500	0	
2.00	3.30	4.20	10.6833	1	X
2.00	3.36	4.40			
2.00	3.40	4.40			
2.10	3.40	4.70			
2.28	3.40	4.70			
2.40	3.43	4.80			
2.45	3.45	4.85			
2.60	3.50	4.87			
2.75	3.50	4.91			
2.80	3.50	6.25			
3.00	3.50	6.30			
3.00	3.50	11.30			
3.08	3.50	23.10R			
3.10	3.50	28.00R			
3.10	3.50	120.00R			
3.10	3.50				
3.10	3.50				
3.10	3.50				
3.10	3.60				
3.14	3.60				
3.20	3.70				
3.20	3.80				
3.20	3.80				
3.20	3.80				
3.20	3.80				
3.20	3.80				

R = REJECTED DATA

TABLE 9

Data Summary by Ampul, Analyses for
Total Mercury in Distilled Water

AMPUL & INCREMENT = 4.1 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	92	RANGE	10.39999	COEF. VAR.	0.33264
TRUE VAL.	4.10	VARIANCE	2.00610	SKWNESS	0.83313
MEAN, ALL	6.23096	STD. DEV.	1.41636	NO. OF CELLS	9
MEAN, RET.	4.25785	CONF. LIM.	± 2.79163 (95 PCT)		
MEDIAN	4.20000				
ACCURACY	3.85005	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.20	4.10	4.80	0.7778	4	XXXX
0.90	4.10	4.95	1.9333	3	XXX
1.11	4.10	5.00	3.0889	12	XXXXXXXXXXXX
1.25	4.10	5.08	4.2444	52	XXXXXXXXXXXX
1.65	4.10	5.10	5.4000	12	XXXXXXXXXXXX
2.10	4.10	5.20	6.5556	2	XX
2.50	4.20	5.40	7.7111	3	XXX
2.60	4.20	5.40	8.8667	0	
2.90	4.20	5.56	10.0222	1	X
3.10	4.20	5.60			
3.21	4.20	5.86			
3.30	4.20	5.89			
3.30	4.20	5.90			
3.40	4.22	6.00			
3.40	4.27	6.70			
3.50	4.29	7.50			
3.50	4.30	7.70			
3.60	4.30	8.00			
3.60	4.30	10.60			
3.70	4.30	16.30R			
3.70	4.30	30.00R			
3.73	4.38	148.00R			
3.80	4.40				
3.80	4.40				
3.80	4.40				
3.80	4.50				
3.80	4.50				
3.90	4.50				
3.90	4.50				
4.00	4.50				
4.00	4.60				
4.00	4.60				
4.00	4.60				
4.10	4.60				
4.10	4.70				

R = REJECTED DATA

TABLE 10

Data Summary by Ampul, Analyses for
Total Mercury in Distilled Water

AMPUL 7 INCREMENT = 8.8 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	90	RANGE	19.45000	COEF. VAR.	0.30721
TRUE VAL.	8.80	VARIANCE	6.78160	SKENNESS	0.23553
MEAN, ALL	12.94298	STD. DEV.	2.60415	NO. OF CELLS	9
MEAN, RET.	8.47665	CONF. LIM.	± 5.13338 (95 PCT)		
MEDIAN	8.70000				
ACCURACY	-3.67439	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.55	8.40	10.00	1.6306	2	XX
2.00	8.40	10.00	3.7917	7	XXXXXXX
3.14	8.50	10.05	5.9528	8	XXXXXXXX
3.30	8.50	10.20	8.1139	39	XXXXXXXXXXXXXXXXXX
3.35	8.56	10.51	10.2750	24	XXXXXXXXXXXXXXXXXX
3.60	8.60	10.60	12.4361	6	XXXXXX
4.20	8.60	10.75	14.5972	0	
4.40	8.70	10.99	16.7583	0	
4.56	8.70	11.00	18.9194	1	X
5.00	8.70	11.00			
6.00	8.80	11.60			
6.00	9.00	11.88			
6.20	9.00	12.00			
6.30	9.00	12.00			
6.80	9.00	13.00			
6.85	9.00	13.20			
7.00	9.00	20.00			
7.20	9.00	36.40R			
7.30	9.10	63.00R			
7.40	9.10	328.00R			
7.43	9.10				
7.50	9.20				
7.50	9.30				
7.70	9.30				
7.80	9.30				
7.90	9.30				
8.00	9.40				
8.00	9.40				
8.00	9.40				
8.10	9.50				
8.20	9.60				
8.20	9.80				
8.30	10.00				
8.30	10.00				
8.35	10.00				

R = REJECTED DATA

TABLE 11

Data Summary by Ampul, Analyses for
Total Mercury in Distilled Water

AMPUL 8 INCREMENT = 9.6 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	92	RANGE	24.42000	COEF. VAR.	0.34549
TRUE VAL.	9.60	VARIANCE	10.49769	SKEWNESS	0.93523
MEAN, ALL	14.06519	STD. DEV.	3.24001	NO. OF CELLS	9
MEAN, RET.	9.37776	CONF. LIM.	± 6.35042 (95 PCT)		
MEDIAN	9.30000				
ACCURACY	-2.31498	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.58	9.00	10.80	1.9367	3	XXX
1.18	9.00	11.00	4.6500	7	XXXXXXX
2.30	9.10	11.00	7.3633	17	XXXXXXXXXXXXXXXXXX
3.59	9.10	11.03	10.0767	49	XXXXXXXXXXXXXXXXXX
4.10	9.10	11.20	12.7900	11	XXXXXXXXXXXX
4.25	9.10	11.40	15.5033	1	X
4.60	9.20	11.85	18.2167	1	X
4.80	9.20	11.96	20.9300	0	
4.80	9.30	12.00	23.6433	1	X
5.20	9.30	12.50			
6.20	9.30	12.80			
7.20	9.50	13.00			
7.30	9.60	13.00			
7.50	9.60	13.25			
7.50	9.60	13.30			
7.60	9.60	13.50			
7.70	9.60	14.00			
7.80	9.70	15.75			
7.89	9.70	18.60			
8.00	9.80	25.00			
8.10	9.80	68.00R			
8.20	9.90	382.00R			
8.20	9.90				
8.30	9.95				
8.34	10.00				
8.40	10.00				
8.48	10.00				
8.80	10.00				
8.80	10.00				
8.80	10.00				
8.90	10.00				
8.90	10.00				
9.00	10.00				
9.00	10.40				
9.00	10.40				

R = REJECTED DATA

TABLE 12

Data Summary by Ampul, Analyses for
in Natural Water

AMPUL 1 INCREMENT = 0.21 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	78	RANGE	1.27000	COEF. VAR.	0.78879
TRUE VAL.	0.21	VARIANCE	0.07598	SKEWNESS	1.44675
MEAN, ALL	0.54243	STD. DEV.	0.27564	NO. OF CELLS	8
MEAN, RET.	0.34945	CONF. LIM.	±0.54761 (95 PCT)		
MEDIAN	0.27000				
ACCURACY	66.40551	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.00	0.26	1.00	0.0794	16	XXXXXXXXXXXXXXXXXX
0.00	0.27	1.20	0.2381	29	XXXXXXXXXXXXXXXXXX
0.00	0.29	1.27	0.3969	11	XXXXXXXXXXXX
0.00	0.30	1.80R	0.5556	7	XXXXXXX
0.03	0.30	2.20R	0.7144	1	X
0.07	0.30	3.35R	0.8731	4	XXXX
0.08	0.30	4.70R	1.0319	3	XXX
0.10	0.30	4.75R	1.1906	2	XX
0.10	0.30				
0.10	0.30				
0.10	0.32				
0.10	0.35				
0.14	0.39				
0.15	0.40				
0.15	0.40				
0.15	0.40				
0.16	0.40				
0.18	0.44				
0.20	0.44				
0.20	0.45				
0.20	0.47				
0.20	0.48				
0.20	0.48				
0.20	0.49				
0.20	0.50				
0.20	0.50				
0.20	0.50				
0.20	0.56				
0.22	0.64				
0.22	0.80				
0.22	0.80				
0.22	0.80				
0.23	0.90				
0.24	1.00				
0.25	1.00				

R = REJECTED DATA

TABLE 13

Data Summary by Ampul, Analyses for
in Natural Water

AMPUL 2 INCREMENT = 0.27 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	82	RANGE	1.20000	COEF. VAR.	0.67494
TRUE VAL.	0.27	VARIANCE	0.07808	SKEWNESS	1.06406
MEAN, ALL	0.65390	STD. DEV.	0.27944	NO. OF CELLS	9
MEAN, RET.	0.41402	CONF. LIM.	±0.55477 (95 PCT)		
MEDIAN	0.32000				
ACCURACY	59.34271	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.00	0.30	1.00	0.0667	7	XXXXXXX
0.00	0.31	1.00	0.2000	21	XXXXXXXXXXXXXXXXXX
0.06	0.31	1.00	0.3333	21	XXXXXXXXXXXXXXXXXX
0.07	0.32	1.00	0.4666	11	XXXXXXXXXXXXX
0.10	0.32	1.05	0.5999	4	XXXX
0.10	0.33	1.10	0.7332	5	XXXXX
0.11	0.35	1.20	0.8665	0	
0.15	0.35	2.09R	0.9998	6	XXXXXX
0.15	0.35	2.60R	1.1331	2	XX
0.16	0.35	3.80R			
0.16	0.40	5.75R			
0.19	0.40	7.50R			
0.20	0.40				
0.20	0.40				
0.20	0.42				
0.20	0.44				
0.20	0.46				
0.20	0.49				
0.20	0.50				
0.21	0.50				
0.21	0.50				
0.23	0.50				
0.24	0.50				
0.24	0.50				
0.25	0.53				
0.25	0.59				
0.26	0.61				
0.26	0.65				
0.27	0.65				
0.27	0.78				
0.28	0.80				
0.30	0.80				
0.30	0.80				
0.30	0.80				
0.30	1.00				

R = REJECTED DATA

TABLE 14

Data Summary by Ampul, Analyses for
in Natural Water

AMPUL 3 INCREMENT = 0.51 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	83	RANGE	3.99000	COEF. VAR.	0.80267
TRUE VAL.	0.51	VARIANCE	0.29254	SKEWNESS	3.32568
MEAN, ALL	1.14505	STD. DEV.	0.54087	NO. OF CELLS	9
MEAN, RET.	0.67384	CONF. LIM.	±1.08031 (95 PCT)		
MEDIAN	0.50500				
ACCURACY	32.12645	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.01	0.50	1.20	0.2317	30	XXXXXXXXXXXXXXXX
0.10	0.50	1.40	0.6750	30	XXXXXXXXXXXXXXXX
0.11	0.50	1.40	1.1183	11	XXXXXXXXXXXX
0.20	0.50	1.44	1.5717	5	XXXXX
0.20	0.51	1.46	2.0050	0	
0.20	0.52	1.70	2.4483	1	X
0.20	0.55	2.40	2.8917	0	
0.22	0.56	4.00	3.3350	0	
0.26	0.56	4.20R	3.7783	1	X
0.28	0.57	4.30R			
0.30	0.60	7.50R			
0.30	0.60	8.00R			
0.32	0.60	18.48R			
0.34	0.60				
0.35	0.62				
0.35	0.64				
0.35	0.65				
0.37	0.66				
0.40	0.69				
0.40	0.70				
0.40	0.70				
0.40	0.75				
0.40	0.77				
0.40	0.80				
0.40	0.82				
0.40	0.93				
0.40	0.95				
0.42	1.00				
0.44	1.00				
0.45	1.00				
0.46	1.05				
0.47	1.06				
0.50	1.10				
0.50	1.10				
0.50	1.10				

R = REJECTED DATA

TABLE 15

Data Summary by Ampul, Analyses for
in Natural Water

AMPUL 4 INCREMENT = 0.60 UG/LITER ORGANIC & INORGANIC MERCURY

N, ALL DATA	80	RANGE	2.30000	COEF. VAR.	0.55003
TRUE VAL.	0.60	VARIANCE	0.15192	SKENNESS	1.32462
MEAN, ALL	1.11749	STD. DEV.	0.38977	NO. OF CELLS	8
MEAN, RET.	0.70864	CONF. LIM.	± 0.77421 (95 PCT)		
MEDIAN	0.60000				
ACCURACY	18.10795	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT FREQ.	HISTOGRAM
			RETAINED DATA ONLY	
0.00	0.60	1.50	0.1438	6 XXXXXX
0.10	0.60	1.60	0.4313	25 XXXXXXXXXXXXXXXX
0.16	0.60	1.70	0.7188	22 XXXXXXXXXXXXXXXX
0.20	0.61	2.30	1.0063	12 XXXXXXXXXXXXXXXX
0.22	0.62	2.66P	1.2938	4 XXXX
0.25	0.64	3.90R	1.5813	4 XXXX
0.30	0.64	4.20R	1.8688	0
0.30	0.65	7.50R	2.1563	1 X
0.35	0.66	8.70R		
0.35	0.69	10.00R		
0.38	0.70			
0.40	0.72			
0.40	0.72			
0.40	0.73			
0.44	0.75			
0.45	0.80			
0.46	0.80			
0.46	0.80			
0.49	0.90			
0.49	0.91			
0.50	0.95			
0.50	0.96			
0.50	1.00			
0.50	1.00			
0.50	1.00			
0.50	1.00			
0.50	1.00			
0.50	1.00			
0.53	1.05			
0.55	1.10			
0.56	1.20			
0.58	1.20			
0.60	1.30			
0.60	1.32			
0.60	1.50			

R = REJECTED DATA

TABLE 16

Data Summary by Ampul, Analyses for
in Natural Water

AMPUL 5 INCREMENT = 3.4 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	83	RANGE	12.37000	COEF. VAR.	0.43743
TRUE VAL.	3.40	VARIANCE	2.22696	SKEWNESS	2.56669
MEAN, ALL	5.38288	STD. DEV.	1.49230	NO. OF CELLS	9
MEAN, RET.	3.41149	CONF. LIM.	± 2.94313 (95 PCT)		
MEDIAN	3.40500				
ACCURACY	0.33800	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.13	3.30	4.60	0.8172	5	XXXXX
0.16	3.40	4.60	2.1916	15	XXXXXXXXXXXXXXXXXX
0.64	3.40	4.70	3.5661	49	XXXXXXXXXXXXXXXXXX
0.85	3.40	4.84	4.9405	9	XXXXXXXXXX
1.36	3.40	4.85	6.3150	1	X
1.70	3.41	5.00	7.6894	0	
1.80	3.48	5.06	9.0639	0	
2.10	3.50	5.40	10.4383	0	
2.10	3.50	7.20	11.8128	1	X
2.10	3.50	12.50			
2.10	3.50	18.86R			
2.10	3.50	30.00R			
2.40	3.50	125.00R			
2.50	3.50				
2.60	3.55				
2.79	3.60				
2.80	3.60				
2.80	3.60				
2.80	3.60				
2.80	3.70				
2.90	3.70				
2.90	3.70				
2.94	3.80				
2.96	3.80				
3.00	3.80				
3.00	3.80				
3.00	3.80				
3.00	3.95				
3.10	4.00				
3.15	4.00				
3.20	4.00				
3.20	4.20				
3.30	4.20				
3.30	4.20				
3.30	4.40				

R = REJECTED DATA

TABLE 17

Data Summary by Ampul, Analyses for
in Natural Water

AMPUL 6 INCREMENT = 4.1 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	80	RANGE	6.33000	COEF. VAR.	0.29282
TRUE VAL.	4.10	VARIANCE	1.24377	SKEWNESS	-0.95121
MEAN, ALL	6.44311	STD. DEV.	1.11524	NO. OF CELLS	8
MEAN, RET.	3.80854	CONF. LIM.	±2.21445 (95 PCT)		
MEDIAN	4.00000				
ACCURACY	-7.10865	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.17	4.00	5.00	0.5657	3	XXX
0.77	4.00	5.20	1.3569	3	XXX
0.83	4.00	5.60	2.1482	4	XXXX
1.10	4.00	5.60	2.9394	9	XXXXXXXXXX
1.70	4.00	5.82	3.7307	27	XXXXXXXXXXXXXXXXXX
1.70	4.00	6.50	4.5219	21	XXXXXXXXXXXXXXXXXX
2.20	4.10	19.00R	5.3132	7	XXXXXXX
2.30	4.10	21.00R	6.1044	2	XX
2.40	4.10	33.00R			
2.50	4.10	153.00R			
2.70	4.10				
2.70	4.20				
3.00	4.20				
3.00	4.20				
3.10	4.22				
3.10	4.25				
3.20	4.30				
3.20	4.30				
3.30	4.30				
3.40	4.30				
3.46	4.30				
3.50	4.40				
3.60	4.40				
3.70	4.50				
3.70	4.50				
3.73	4.50				
3.77	4.50				
3.90	4.58				
3.90	4.60				
3.90	4.70				
3.90	4.80				
4.00	4.80				
4.00	4.95				
4.00	5.00				
4.00	5.00				

R = REJECTED DATA

TABLE 18

Data Summary by Ampul, Analyses for
in Natural Water

AMPUL 7 INCREMENT = 8.8 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	80	RANGE	27.47000	COEF. VAR.	0.42143
TRUE VAL.	8.80	VARIANCE	13.65052	SKEWNESS	2.00048
MEAN, ALL	13.62260	STD. DEV.	3.69466	NO. OF CELLS	8
MEAN, RET.	8.76678	CONF. LIM.	± 7.24153 (95 PCT)		
MEDIAN	8.50000				
ACCURACY	-0.37750	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ.	HISTOGRAM
			RETAINED DATA ONLY		
0.53	8.40	12.00	2.2469	7	XXXXXXX
1.88	8.40	12.00	5.6807	12	XXXXXXXXXXXX
2.45	8.43	13.00	9.1144	46	XXXXXXXXXXXXXXXXXXXX
3.00	8.50	13.00	12.5482	10	XXXXXXXXXXXX
3.22	8.50	13.80	15.9819	1	X
3.42	8.50	15.75	19.4157	0	
3.90	8.50	21.30	22.8494	1	X
4.50	8.60	28.00	26.2832	1	X
4.80	8.60	66.00R			
6.10	8.70	340.00R			
6.30	8.80				
6.36	8.90				
6.50	8.90				
6.60	9.00				
6.80	9.00				
7.20	9.00				
7.21	9.00				
7.30	9.00				
7.34	9.10				
7.40	9.10				
7.50	9.40				
7.76	9.45				
7.80	9.50				
7.80	9.70				
8.00	9.80				
8.00	10.05				
8.10	10.30				
8.10	10.40				
8.20	10.60				
8.20	10.70				
8.30	11.00				
8.30	11.00				
8.30	11.03				
8.35	11.20				
8.40	11.98				

R = REJECTED DATA

TABLE 19

Data Summary by Ampul, Analyses for
in Natural Water

RECOVERY OF INCREMENT FROM NATURAL WATER

AMPUL 8 INCREMENT = 9.6 UG/LITER ORGANIC + INORGANIC MERCURY

N, ALL DATA	79	RANGE	25.76000	COEF. VAR.	0.39210
TRUE VAL.	9.60	VARIANCE	12.72246	SKEWNESS	1.11538
MEAN, ALL	14.57516	STD. DEV.	3.56685	NO. OF CELLS	8
MEAN, RET.	9.09660	CONF. LIM.	± 6.99103 (95 PCT)		
MEDIAN	9.20000				
ACCURACY	-5.24370	PCT RELATIVE ERROR			

DATA IN ASCENDING ORDER

MIDPOINT FREQ. HISTOGRAM
RETAINED DATA ONLY

0.54	9.05	12.80	2.1500	5	XXXXX
1.18	9.10	13.27	5.3700	9	XXXXXXXXXX
1.98	9.10	14.00	8.5900	44	XXXXXXXXXXXXXXXXXX
3.35	9.20	14.50	11.8100	14	XXXXXXXXXXXXXXXXXX
3.52	9.20	15.40	15.0300	3	XXX
3.80	9.20	17.00	18.2500	1	X
4.00	9.40	26.30	21.4700	0	
4.10	9.40	72.00R	24.6900	1	X
5.00	9.50	379.00R			
5.10	9.50				
5.40	9.50				
6.20	9.60				
6.20	9.60				
6.72	9.60				
7.20	9.70				
7.30	9.80				
7.50	9.80				
7.60	9.80				
7.80	9.95				
7.80	10.00				
7.96	10.00				
8.00	10.00				
8.10	10.00				
8.10	10.50				
8.30	10.70				
8.30	10.70				
8.34	10.80				
8.50	11.00				
8.70	11.00				
8.80	11.80				
8.90	11.80				
9.00	11.98				
9.00	12.00				
9.00	12.00				
9.00	12.60				

R = REJECTED DATA

Statistical Summaries

A statistical summary is given in Tables 20 and 21 for each sample. Most of the statistics have been selected from Tables 4 through 19 to allow a convenient comparison of the effect that differences in concentration level and background water had on the retained data.

Single-Analyst Precision

In Tables 20 and 21, the standard deviations (S) indicate the dispersion expected among values generated from a group of laboratories. This represents the broad error in any mass of data collected in a collaborative study. However, the measure of how well an individual analyst can expect to perform in his own laboratory is another important measure of precision. This single-analyst precision is measured here as the S_r value. It was defined by Youden (2) as

$$S_r = \sqrt{\frac{\sum (D_i - \bar{D})^2}{2(n - 1)}}$$

where

n = the number of paired observations.

D_i = the difference between observation for a sample pair.

$\bar{D}$ = the average value for D_i .

Youden's S_r calculation permits a measure of precision without duplication and hopefully avoids the well-intentioned manipulation of data that can occur in a laboratory doing replicate determinations.

Statements of Method Precision

Linear regressions were performed on the overall and single-analyst precision estimates shown in Tables 20 and 21 for the cold vapor method of determining mercury in distilled and natural waters. Plots of these regressions are shown in Figures 1 and 2. Mathematical expressions of the precision statements for mean recovery ($\bar{X}$) from 0.2-10 $\mu\text{g/liter}$ of total mercury in distilled and natural waters are given as follows:

Distilled Water:

Overall precision (S) = $0.2454 + 0.2922 \bar{X}$

Single-analyst precision (S_r) = $0.3117 + 0.0718 \bar{X}$

TABLE 20

STATISTICAL SUMMARY

Recovery of Total Mercury from Distilled and Natural Waters

STATISTICAL PARAMETERS	DISTILLED WATER		NATURAL WATER		DISTILLED WATER		NATURAL WATER	
	SAMPLE 1	SAMPLE 2	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 3	SAMPLE 4
True Value, $\mu\text{g/l}$	.21	.27	.21	.27	.51	.60	.51	.60
Mean Recovery, $\mu\text{g/l}$ ($\bar{X}$)	.418	.450	.349	.414	.653	.744	.674	.709
Accuracy as Σ Rel. Error	98.9	66.5	66.4	53.3	28.1	24.0	32.1	18.1
Standard Dev., $\mu\text{g/l}$ (S)	.279	.325	.276	.279	.376	.466	.541	.390
Relative Dev., Σ	66.9	72.2	78.9	67.5	57.5	62.6	80.3	55.5
Range, $\mu\text{g/l}$	1.60	1.80	1.27	1.20	2.26	2.97	3.99	2.30
Single-Analyst Standard Dev., $\mu\text{g/l}$ (S_F)	0.19		0.16		0.36		0.16	
Single-Analyst Relative Dev., Σ	44		42		51		23	

TABLE 21

STATISTICAL SUMMARY

Recovery of Total Mercury from Distilled and Natural Waters

STATISTICAL PARAMETERS	DISTILLED WATER		NATURAL WATER		DISTILLED WATER		NATURAL WATER	
	SAMPLE 5	SAMPLE 6	SAMPLE 5	SAMPLE 6	SAMPLE 7	SAMPLE 8	SAMPLE 7	SAMPLE 8
True Value, $\mu\text{g/l}$	3.4	4.1	3.4	4.1	8.8	9.6	8.8	9.6
Mean Recovery, $\mu\text{g/l}$ ($\bar{X}$)	3.40	4.26	3.41	3.81	8.48	9.38	8.77	9.10
Accuracy as % Rel. Error	0.03	3.85	0.34	-7.11	-3.7	-2.3	-0.4	-5.2
Standard Dev., $\mu\text{g/l}$ (S)	1.29	1.42	1.49	1.12	2.60	3.24	3.69	3.57
Relative Dev., %	37.9	33.2	43.7	29.3	30.7	34.5	42.1	39.2
Range, $\mu\text{g/l}$	11.1	10.4	12.4	6.3	19.4	24.4	27.5	25.8
Single-Analyst Standard Dev., $\mu\text{g/l}$ (S_r)	0.79		0.36		0.89		1.39	
Single-Analyst Relative Dev., %	20		10		10		16	

FIGURE 1

Linear Regression Plot of Precision in Distilled Water

The precision of this method for total mercury in distilled water samples, within the recovery range of 0.2-10 $\mu\text{g/liter}$, may be expressed as follows:

$$S = 0.2454 + 0.2922 \bar{X}$$

$$S_r = 0.3117 + 0.0718 \bar{X}$$

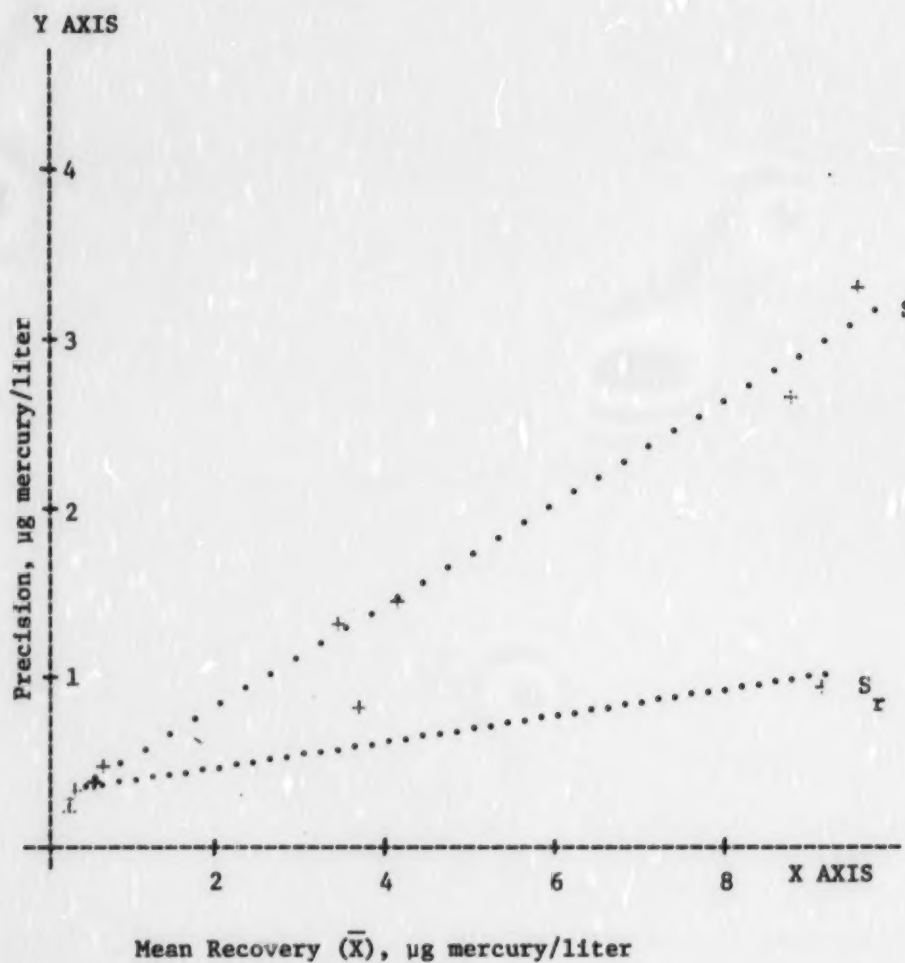


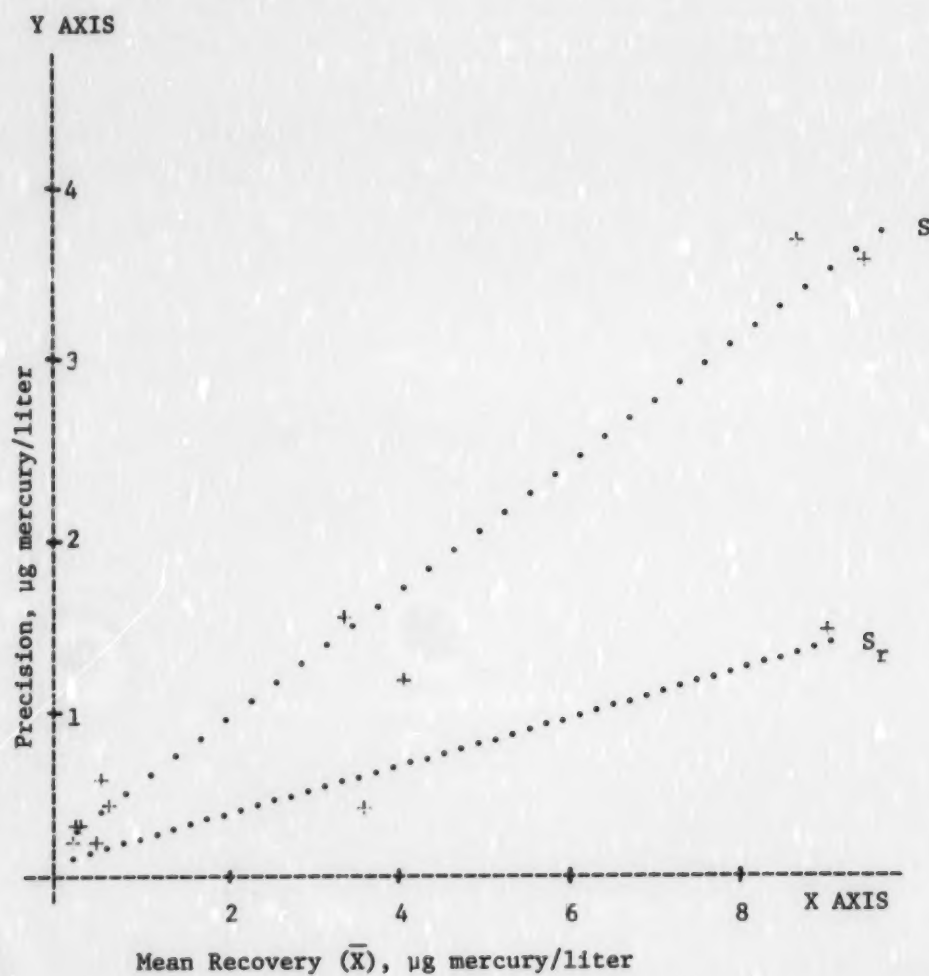
FIGURE 2

Linear Regression Plot of Precision in Natural Water

The precision of this method for total mercury in natural water samples, within the recovery range of 0.2-10 $\mu\text{g/liter}$, may be expressed as follows:

$$S = 0.1661 + 0.3647 \bar{X}$$

$$S_r = 0.0465 + 0.1379 \bar{X}$$



Natural Water:

$$\text{Overall precision (S)} = 0.1661 + 0.3647 \bar{X}$$

$$\text{Single-analyst precision (S}_r\text{)} = 0.0465 + 0.1379 \bar{X}$$

Statements of Method Accuracy

Linear regressions were performed on the mean recovery estimates shown in Tables 20 and 21 for the cold vapor method of determining mercury in distilled and natural waters. Plots of these regressions are shown in Figures 3 and 4. Mathematical expressions of the mean recovery for 0.2-10 µg/liter of total mercury in distilled and natural waters are given as follows:

Distilled Water:

$$\text{Mean Recovery, } \bar{X} = 0.2028 + 0.9517 (\text{True Concentration})$$

Natural Water:

$$\text{Mean Recovery, } \bar{X} = 0.1373 + 0.9508 (\text{True Concentration})$$

Two-Sample (Youden) Charts

The retained data were plotted according to the method of Youden and are shown in Figures 5 through 12. Two results for each sample pair were used respectively as the x and y coordinates to plot a single point for each analyst. The plot of points for each sample pair shows the performance of the method for that concentration level.

If random errors were largely responsible for the spread of results around the true values, the data on a plot would be equally distributed among the four quadrants (+ +), (- +), (- -) and (+ -). However, if systematic error influences the method more, the values are not randomly distributed but are grouped along a 45° slope line in the (- -) and (+ +) quadrants. This occurs because an analyst tends to get either high or low results on both samples in a pair, forming an elliptical pattern on a 45° slope. If an analyst shows large systematic or random error relative to other data, his plot points will be far removed from the general cluster. Extreme values suggest a procedure or instrument out of control. If the method of analysis is inherently imprecise there will be a general scatter of data points away from the 45° line. A significant bias or interference in the method will cause the general grouping to be low (- -) or high (+ +).

The presence of a number of values greater than the true values crowded the plots of points which were less than the true values. In order to present these points more fairly, scale units for the plots were selected which would place the true value at least one-third of the

distance from the origin. This arbitrary rule worked well on all data plots, presenting a reasonable spread of data points over each chart and providing an interpretable representation of method performance. Data which were extremely high are shown as greater than (>) values in the upper right-hand corner of each plot.

FIGURE 3

Linear Regression Plot of Accuracy in Distilled Water

Accuracy as the mean recovery of this method for total mercury in distilled water samples, within the true concentration range of 0.2-10 µg/liter, may be expressed as follows:

$$\text{Mean Recovery} = 0.2028 + 0.9517 (\text{True Concentration})$$

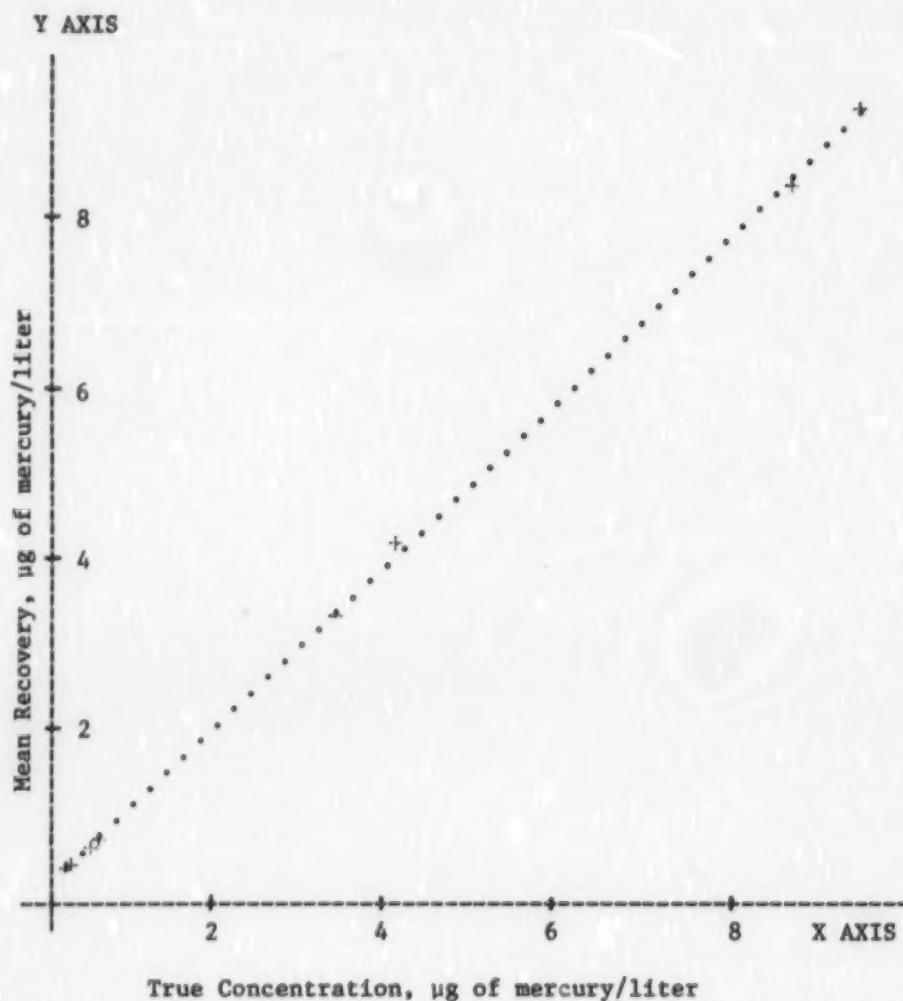


FIGURE 4

Linear Regression Plot of Accuracy in Natural Water

Accuracy as the mean recovery of this method for total mercury in natural water samples, within the true concentration range of 0.2-10 $\mu\text{g/liter}$, may be expressed as follows:

$$\text{Mean Recovery} = 0.1373 + 0.9508 (\text{True Concentration})$$

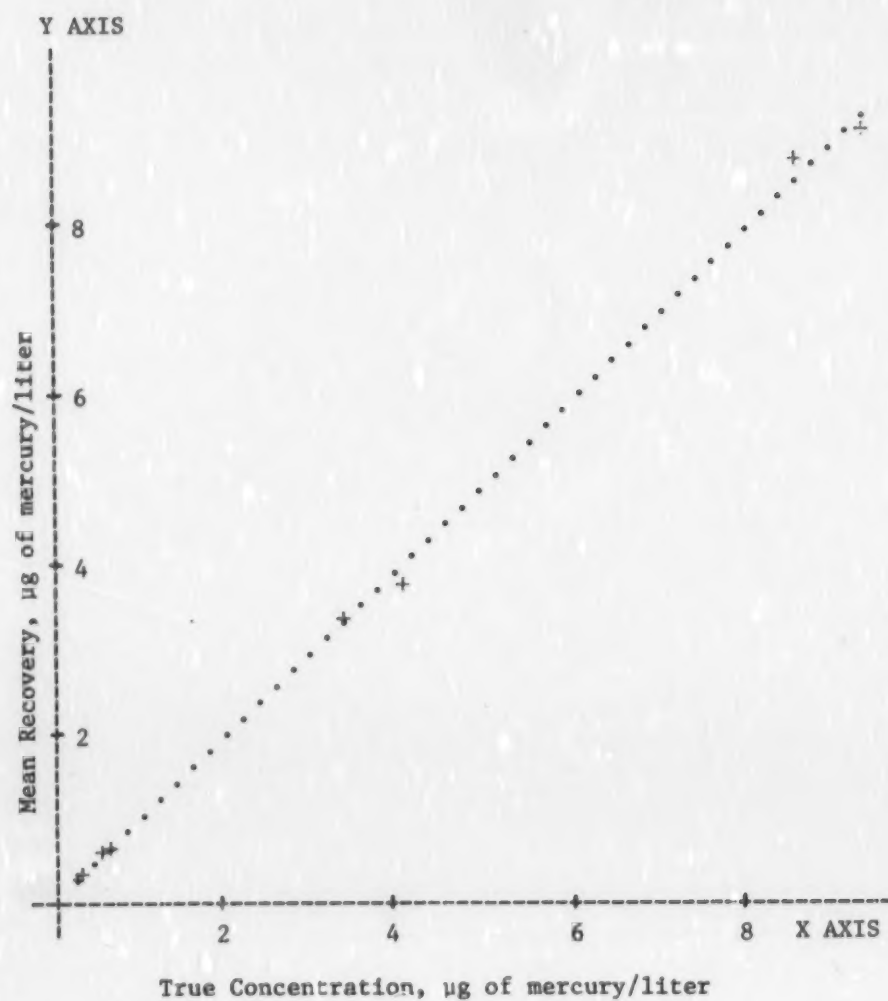


FIGURE 5

Two Sample Chart for Recovery of Total Mercury, $\mu\text{g/liter}$

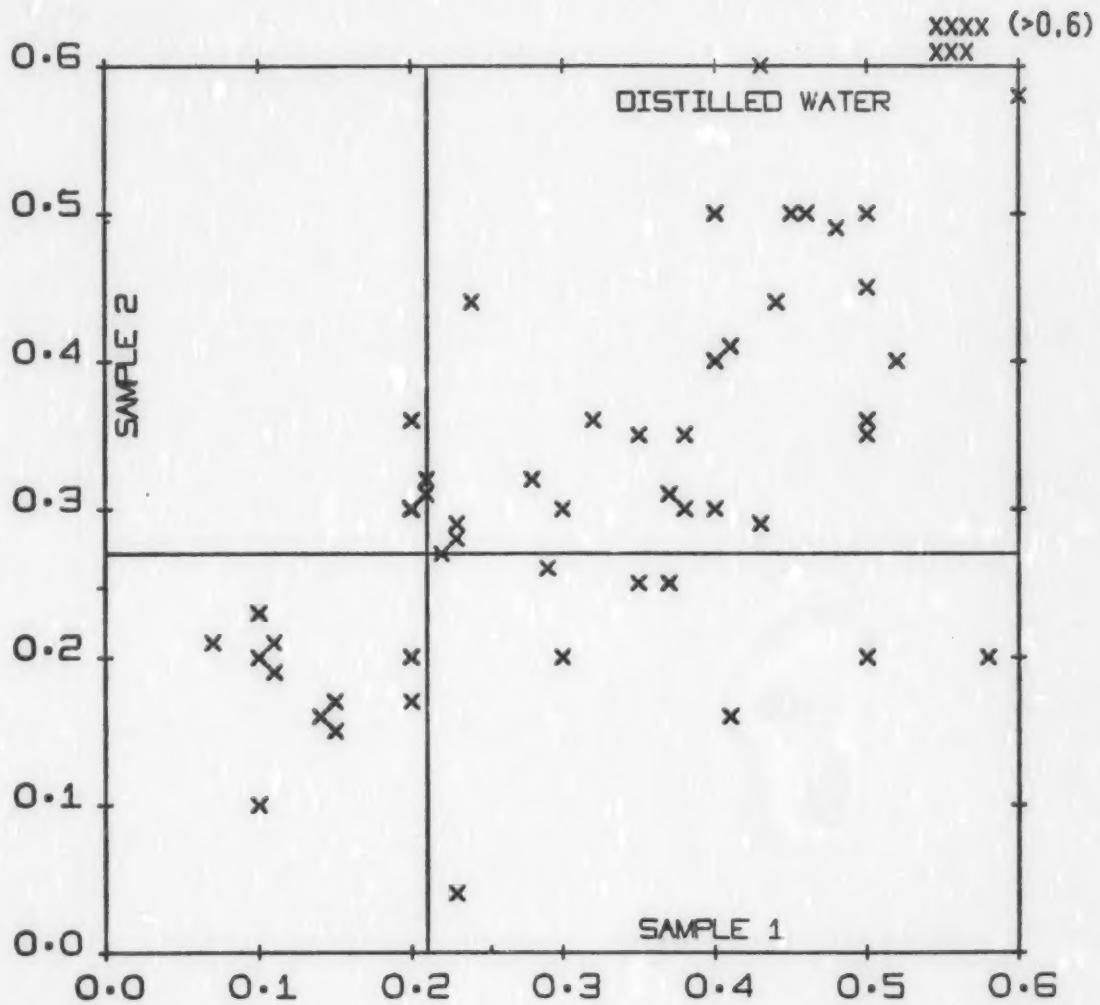


FIGURE 6

Two Sample Chart for Recovery of Total Mercury, $\mu\text{g/liter}$

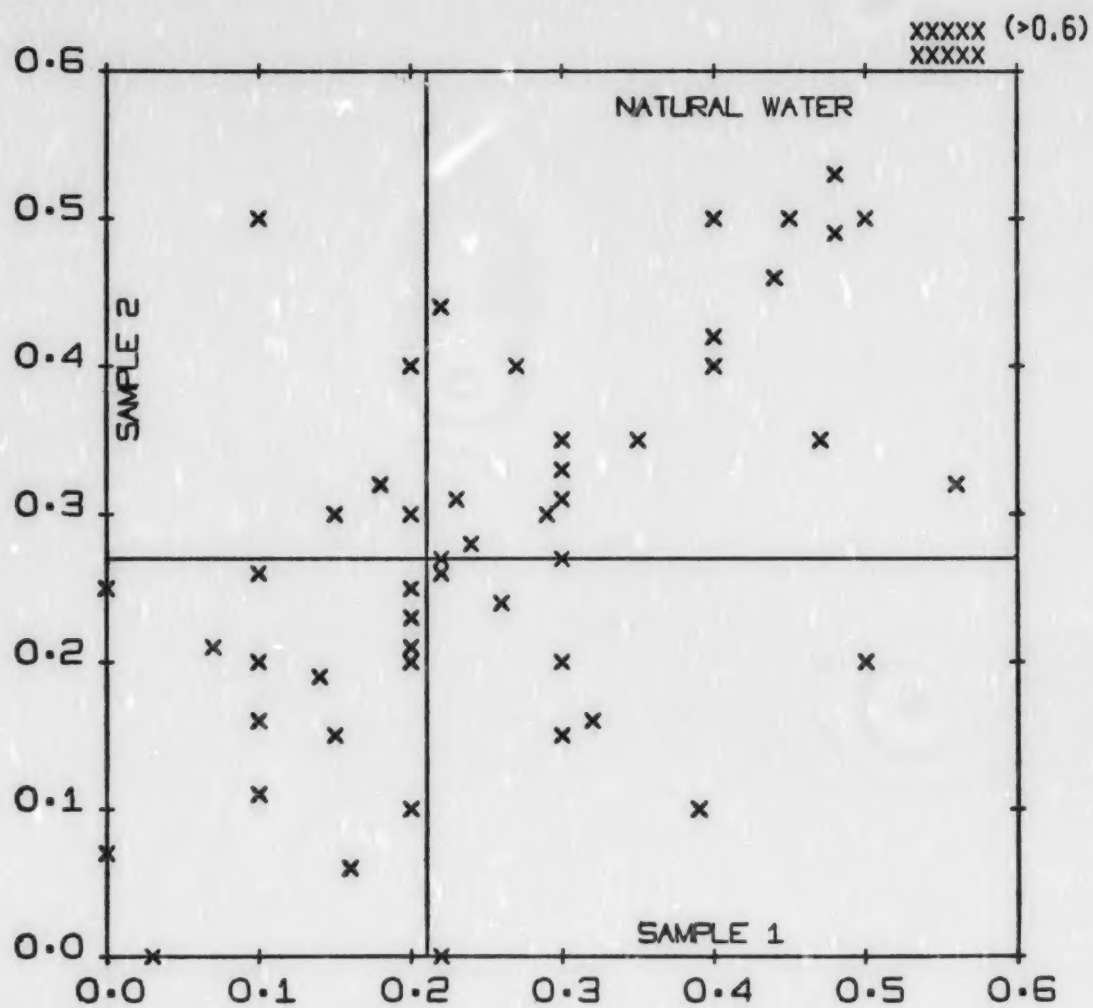


FIGURE 7

Two Sample Chart for Recovery of Total Mercury, $\mu\text{g}/\text{liter}$

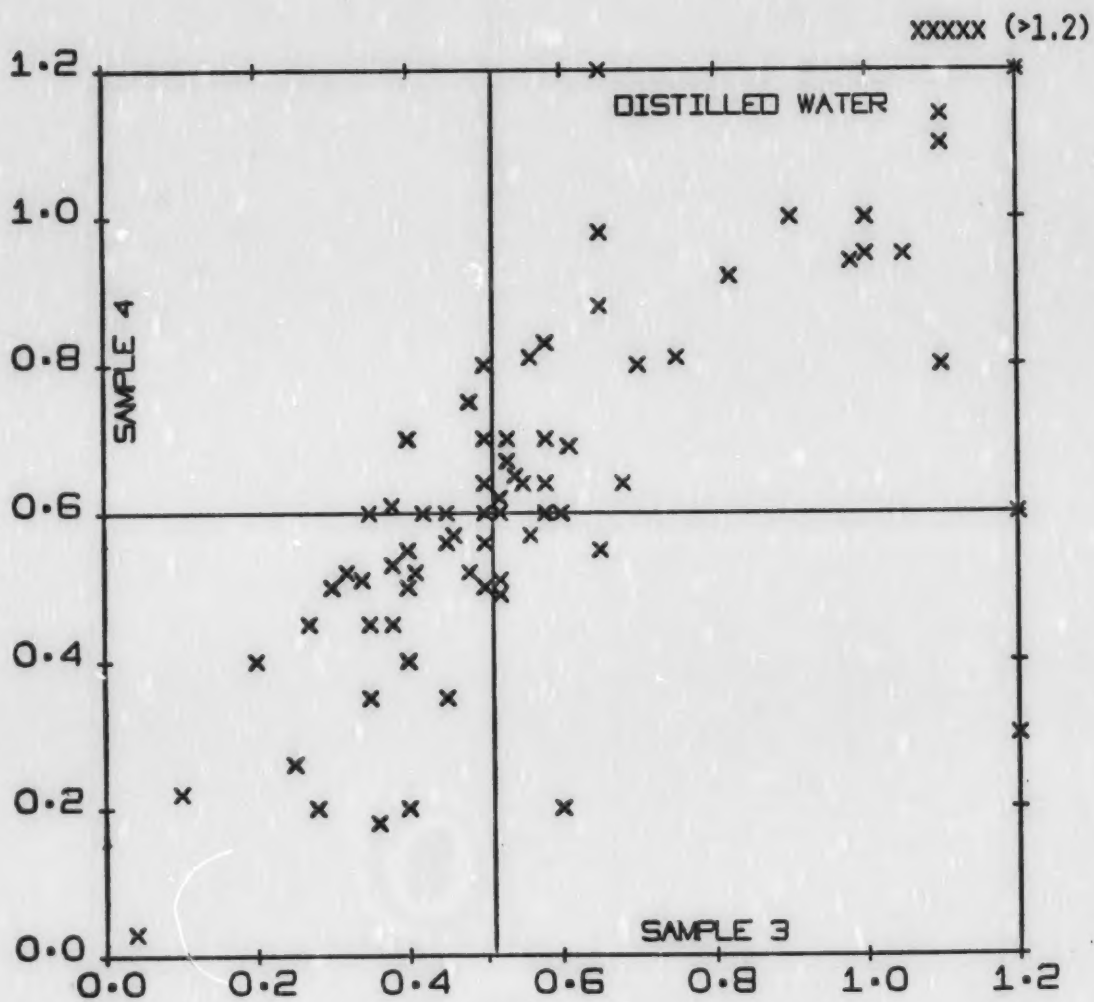


FIGURE 8

Two Sample Chart for Recovery of Total Mercury, $\mu\text{g/liter}$

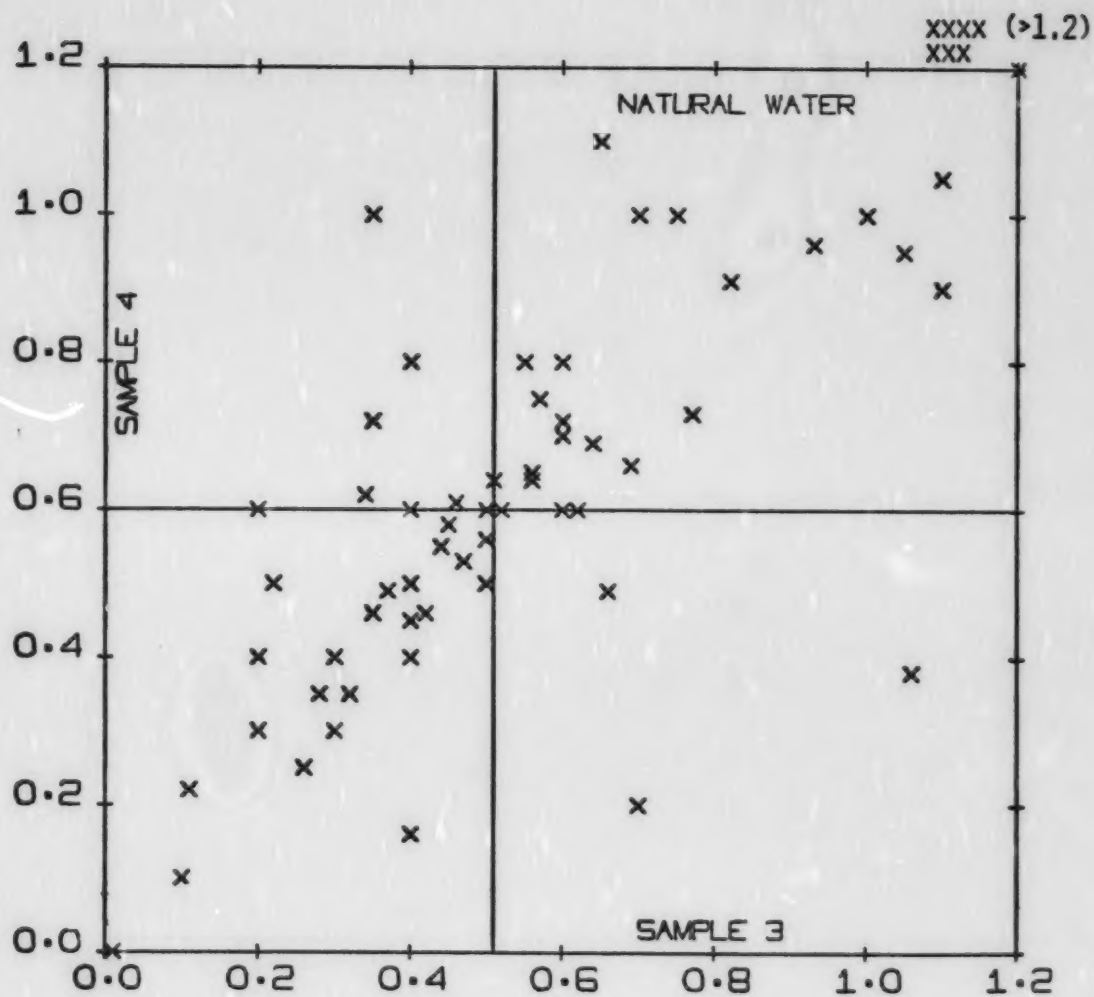


FIGURE 9

Two Sample Chart for Recovery of Total Mercury, $\mu\text{g/liter}$

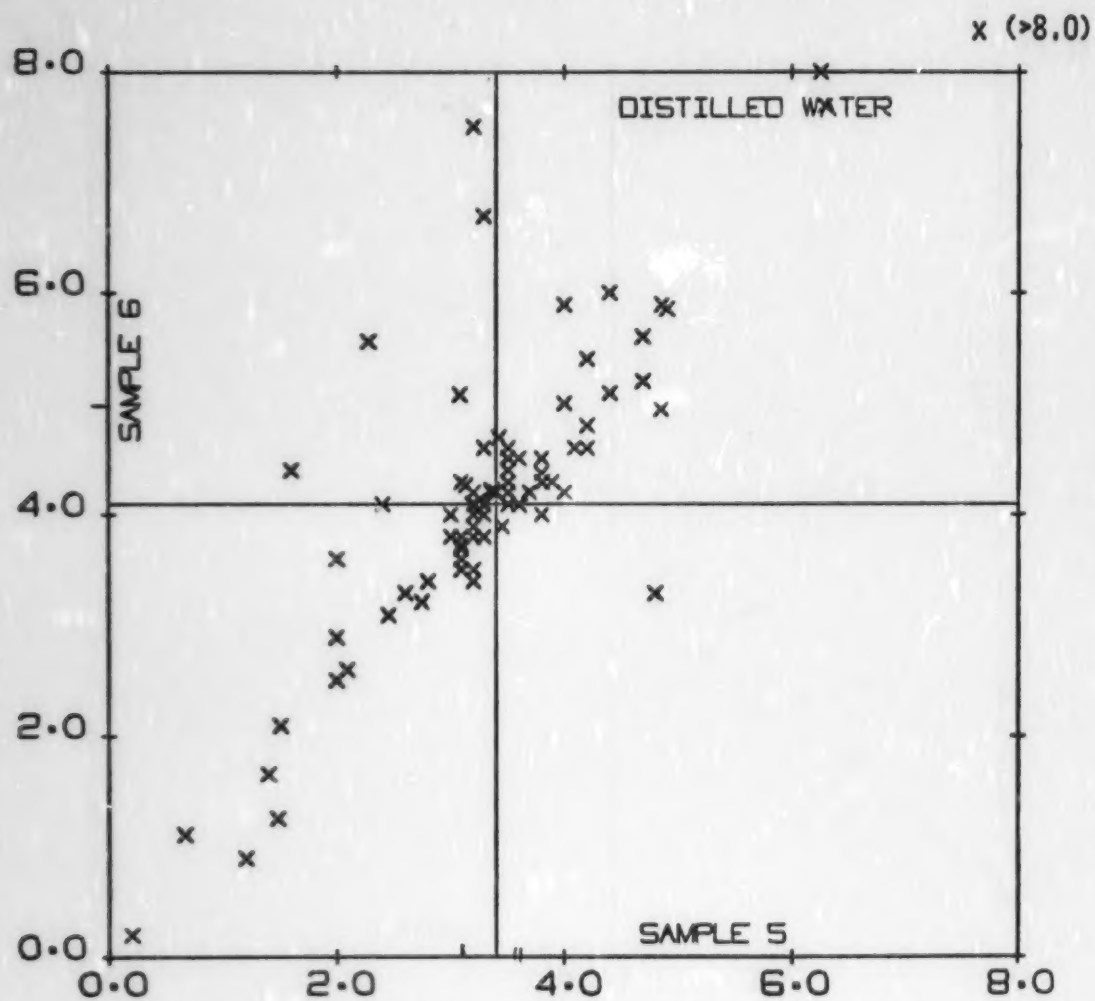


FIGURE 10

Two Sample Chart for Recovery of Total Mercury, $\mu\text{g/liter}$

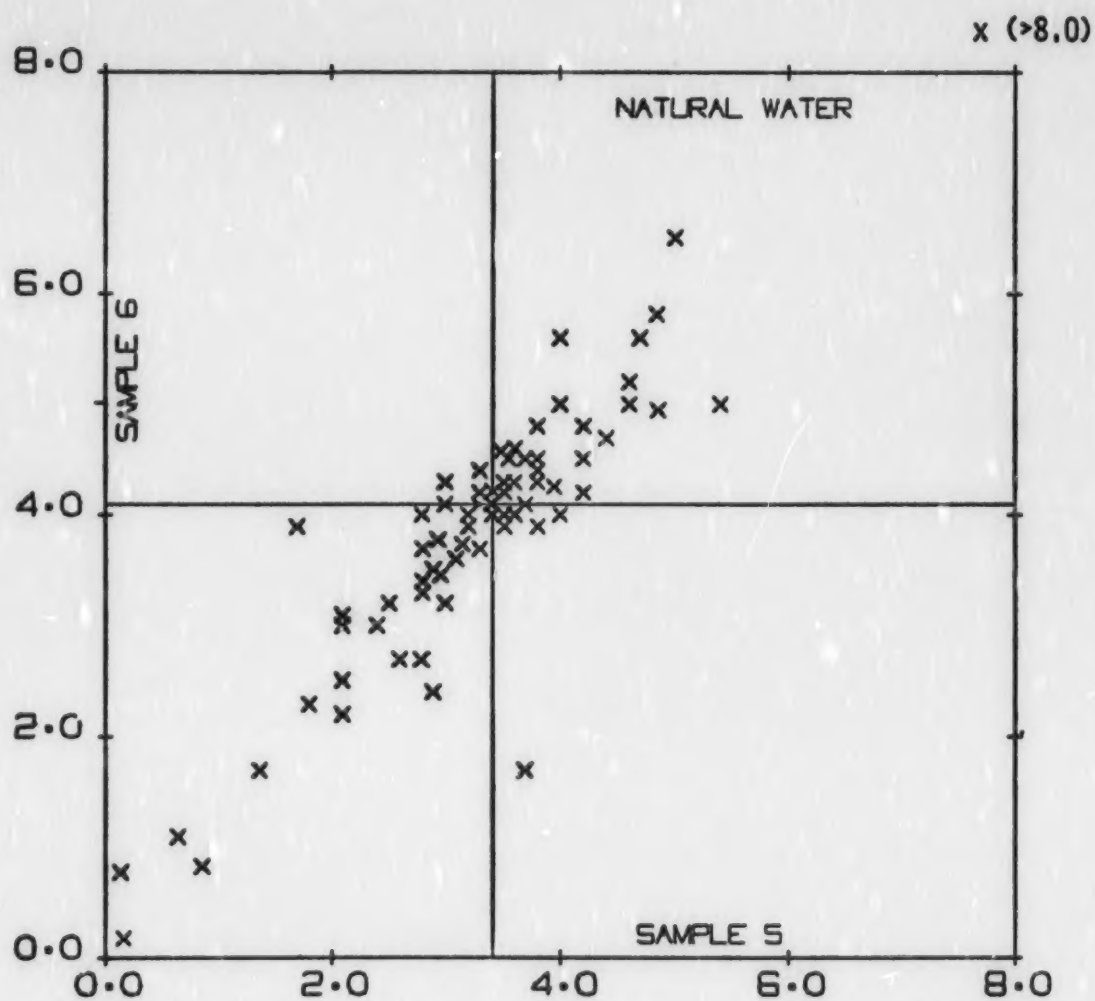


FIGURE 11

Two Sample Chart for Recovery of Total Mercury, $\mu\text{g/liter}$

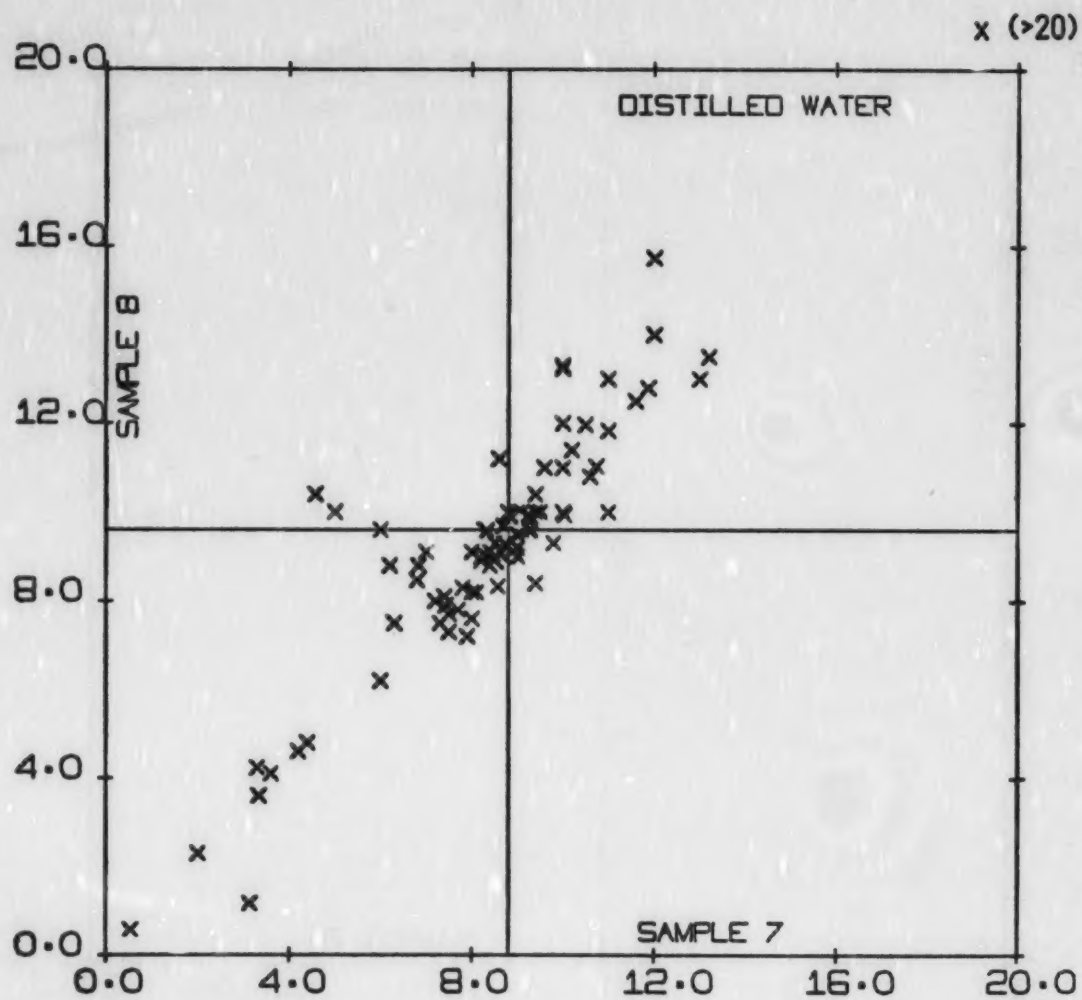
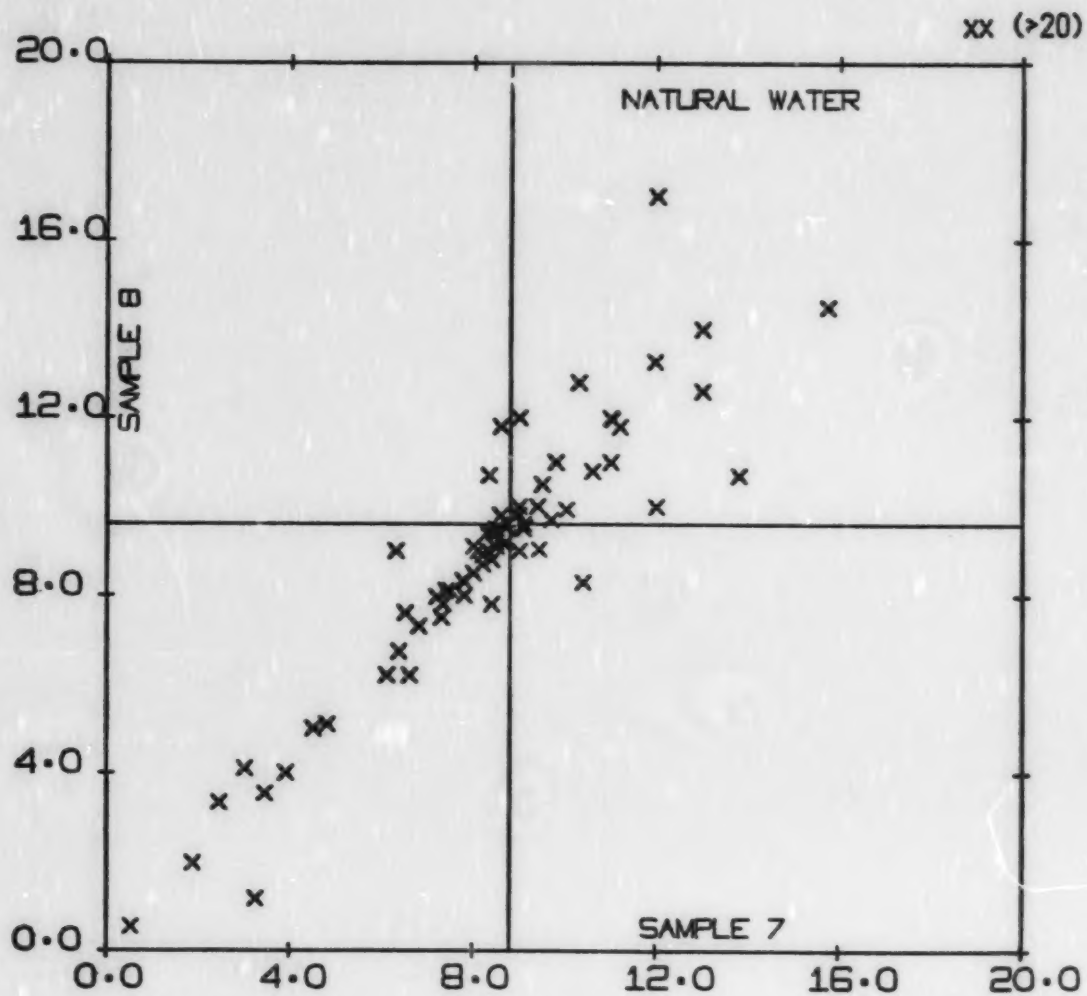


FIGURE 12

Two Sample Chart for Recovery of Total Mercury, $\mu\text{g/liter}$



DISCUSSION AND CONCLUSIONS

Throughout the 0.2-10 $\mu\text{g/liter}$ concentration range tested, mercury was detected and measured using the cold vapor procedure of Kopp (1).

In describing method performance, it has been common to assume that statistics such as mean recovery ($\bar{X}$), standard deviation (S) and single-analyst standard deviation (S_r) are: 1) constants which are independent of the true concentration level or 2) uniform percentages of the true concentration. Tables 20 and 21 show that neither of these assumptions is valid within the concentration range studied. As a matter of fact, for most studies, whenever the concentration range approaches the detection limit these assumptions seem to be invalid. An alternative is to assume that some linear relationship exist between the statistics and the true concentration level. If this is true, then regression equations of the form $Y = aX + b$ will provide good predictions of the method statistics. Please note that the earlier two assumptions are really special cases of the linear assumption.

In this study, the regression equation plots in Figures 1 through 4 fit the points well enough to justify a linear assumption and should, therefore, prove useful for predicting the statistics of this method within the 0.2-10 $\mu\text{g/liter}$ range studied.

Another interesting observation that can be made from Tables 20 and 21 and Figures 1 through 4 is that the type of background water did not have any dramatic effect upon the method statistics. This indicates that the method is not sensitive to natural interferences. However, since few analysts used marine waters or industrial effluents, this conclusion is limited to natural surface waters such as rivers and lakes.

Visual interpretation of the Youden plots (Figures 5-12) leads to a better understanding of the method precision and bias statistics in Tables 20 and 21 and Figures 1 through 4. First notice that the points tend to approach the hypothetical 45 degree line as the concentration level increases. This indicates less relative influence attributable to random error and thereby verifies the decreasing single-analyst relative deviation. Next, note that the points generally tend to form a denser cluster as the concentration level increases. This verifies the decreasing relative deviation values presented in Tables 20 and 21. Also, note that points away from the intersection of the true concentration lines tend to be high for the lower two concentration levels (0.2-0.6 $\mu\text{g/liter}$) and low for the higher two concentration levels (3-10 $\mu\text{g/liter}$). This verifies the decreasing percent relative error values in Tables 20 and 21.

In conclusion, the vigorous digestion procedure using permanganate, persulfate and heat as specified in the method, successfully reduces the organic mercury to a measurable form.

The precision and accuracy of the method for distilled water and natural water samples follows:

Distilled Water:

$$\text{Precision } S = 0.2454 + 0.2922 \bar{X}$$

$$S_r = 0.3117 + 0.0718 \bar{X}$$

Accuracy

$$\text{Mean Recovery, } \bar{X} = 0.2028 + 0.9517 (\text{conc})$$

Natural Water:

$$\text{Precision } S = 0.1661 + 0.3647 \bar{X}$$

$$S_r = 0.0465 + 0.1379 \bar{X}$$

Accuracy

$$\text{Mean Recovery, } \bar{X} = 0.1373 + 0.9508 (\text{conc})$$

REFERENCES

1. Kopp, J. F., M. C. Longbottom and L. B. Lobring, 1972. Cold Vapor Method for the Determination of Mercury, J A W W A, Vol. 64, No. 1, pp. 20-25.
2. Youden, W. J., 1967. Statistical Technique for Collaborative Tests, Association of Official Analytical Chemists, Inc., Washington, D.C.

APPENDIX

Proposed Standard Method of Test for Total Mercury in Water (1)

1. Scope

1.1 This method describes a procedure for the determination of total mercury in water in the range of 0.2-10.0 $\mu\text{g Hg/liter}$. It consists of a wet chemical oxidation which converts all mercury to the mercuric ion; reduction of mercuric ions to metallic mercury, followed by a cold vapor atomic absorption (AA) Analysis (2, 3).

1.2 The method is applicable to fresh waters, saline waters, and industrial and sewage effluents.

1.3 Both organic and inorganic mercury compounds may be analyzed by this procedure if they are first converted to mercuric ions. Potassium permanganate in acid solution oxidizes some organomercury compounds but studies have shown that several methyl and phenyl mercury compounds are only partially oxidized by this method. However, using potassium persulfate and potassium permanganate as oxidants, and a digestion temperature of 95 C, approximately 100% recovery of these compounds can be obtained (3, 4).

1.4 The range of the method may be varied through instrument and/or recorder expansion and by using a larger volume of sample.

1.5 A method for the disposal of mercury containing wastes is also presented (Appendix A1).

2. Summary of Method

2.1 The cold vapor AA procedure is a physical method based on the absorption of ultraviolet radiation at a wavelength of 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in either a closed recirculating system or an open one-pass system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration.

3. Significance

3.1 The cold vapor AA measurement portion of this method is applicable to the analysis of materials other than water (sediments, biological materials, tissues, etc.) if, and only if, an initial procedure for digesting and oxidizing the sample is carried out, insuring that the mercury in the sample is converted to the mercuric ion, and is dissolved in aqueous media (3, 6).

4. Definitions

4.1 For definitions of terms used in this method, refer to ASTM Definitions D1129, Terms Relating to Water (7).

5. Interference

5.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/liter of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water (3).

5.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/liter had no effect on the recovery of mercury from spiked samples (3).

5.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation at 253.7 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the reaction flask must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

5.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. If this is expected, the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is, without the stannous sulfate. The true mercury value can then be obtained by subtracting the two values.

6. Apparatus

6.1 See Figure 1 for the schematic of the closed recirculating system and Figure 2 for the open one-pass system.

6.2 Atomic Absorption Spectrophotometer - Any commercial atomic absorption instrument is suitable if it has an open burner head area in which to mount an absorption cell, and if it provides the sensitivity and stability for the analyses. Also instruments designed specifically for the measurement of mercury using the cold vapor technique in the working range specified are commercially available and may be substituted.

6.3 Mercury Hollow Cathode Lamp

6.4 Recorder - Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

6.5 Absorption Cell - See Figure 3 - The cell is constructed from glass or plexiglass tubing 25.4 mm O.D. x 114 mm (Note 1). The ends are ground perpendicular to the longitudinal axis and quartz window (25.4 mm diameter x 1.6 mm thickness) are cemented in place. Gas inlet and outlet ports (6.4 mm diameter) are attached approximately 12 mm from each end. The cell is strapped to a support and aligned in the light beam to give maximum transmittance.

Note 1 - An all glass absorption cell, 18 mm O.D. by 200 mm, with inlet 12 mm from the end, 18 mm O.D. outlet in the center, and with quartz windows has been found suitable.

6.6 Air Pump - Any peristaltic pump, with electronic speed control, capable of delivering 1 liter of air per minute may be used. (Regulated compressed air can be used in an open one-pass system).

6.7 Flowmeter - Any flowmeter capable of measuring an air flow of 1 liter per minute is suitable.

6.8 Aeration Tubing - A straight glass frit having a coarse porosity is used in the reaction flask. A clear flexible vinyl plastic tubing such as Tygon, is used for passage of the mercury vapor from the reaction flask to the absorption cell.

6.9 Drying Tube - 150 mm x 18 mm diameter tube containing 20 grams of magnesium perchlorate. A small reading lamp with 60w bulb may also be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 C above ambient.

6.10 Reaction Flask - Either a 300 ml B.O.D. bottle or 250 ml erlenmeyer flask fitted with a rubber stopper may be used.

7. Reagents

7.1 Purity of Reagents - Reagent grade chemicals, or equivalent, as defined in ASTM Methods E 200, for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis (7), shall be used in this test.

7.2 Purity of Water - Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specification D1193, for Reagent Water, Type I (7).

7.3 Mercury Standard Solutions

7.3.1 Mercury, Stock Standard Solution (1 ml = 1 mg Hg) - Dissolve 0.1354 grams of mercuric chloride (HgCl_2) in 75 ml of distilled water containing 10 ml of concentrated nitric acid and dilute to 100 ml in a volumetric flask.

7.3.2 Mercury, Intermediate Standard Solution (1 ml = 10 µg Hg) - Add 10 ml of the stock mercury solution to distilled water containing 2 ml of concentrated nitric acid and dilute to 1 liter. Prepare fresh daily.

7.3.3 Mercury Working Standard Solution (1 ml = 0.1 µg Hg) - Add 10 ml of the intermediate mercury standard to distilled water containing 2 ml of concentrated nitric acid and dilute to 1 liter. Prepare fresh daily.

7.4 Nitric Acid (Sp gr 1.42) - Concentrated nitric acid (HNO_3), reagent grade.

Note 2 - If a high reagent blank is obtained, the reagent grade HNO_3 will have to be distilled or a spectro-grade acid will have to be used.

7.5 Potassium Permanganate Solution (50 g/liter) - Dissolve 50 grams of potassium permanganate (KMnO_4) in distilled water and dilute to one liter.

7.6 Potassium Persulfate Solution (50 g/liter) - Dissolve 50 grams of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) in distilled water and dilute to one liter.

7.7 Sodium Chloride - Hydroxylamine Sulfate Solution (120 g/liter) - Dissolve 120 grams of sodium chloride (NaCl) and 120 grams of hydroxylamine sulfate [$(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$] in distilled water and dilute to one liter.

7.8 Stannous Sulfate Solution (100 g/liter) - Dissolve 100 grams of stannous sulfate (SnSO_4) in distilled water containing 14 ml of concentrated sulfuric acid and dilute to one liter. This mixture is a suspension and should be stirred continuously during use.

7.9 Sulfuric Acid (Sp gr 1.84) - Concentrated sulfuric acid (H_2SO_4), reagent grade.

8. Sampling

8.1 Collect the samples in accordance with the applicable method of American Society for Testing and Materials, as follows:

- D510 - Sampling Industrial Water (7)
- D860 - Sampling Water from Boilers (7)
- D1496 - Sampling Homogenous Industrial Waste Water (7)

8.2 Samples should be collected in acid-washed glass or high density polyethylene bottles. Samples could be analyzed within 38 days if collected in glass bottles, and within 13 days if collected in polyethylene bottles (8).

8.3 Samples should be preserved with concentrated nitric acid to a pH of 2 or less immediately at the time of collection, normally about 2 ml/liter. If only dissolved mercury is to be determined, the sample should be filtered through a 0.45 μ membrane filter using an all glass filtering apparatus before acidification.

9. Calibration

9.1 Transfer 0, 1.0, 2.0, 5.0 and 10.0 ml aliquots of the working mercury solution containing 0-1.0 μ g of mercury to a series of reaction flasks. Add enough distilled water to each flask to make a total volume of 100 ml. Mix thoroughly and add 5 ml of concentrated sulfuric acid and 2.5 ml of nitric acid to each flask (Note 3).

Add 15 ml of KMnO_4 solution to each bottle and allow to stand at least 15 minutes. Add 8 ml of potassium persulfate to each flask and heat for two hours in a water bath at 95 C. Cool to room temperature and add 6 ml of sodium chloride--hydroxylamine sulfate solution to reduce the excess permanganate. After waiting 30 seconds treat each flask individually by adding 5 ml of the stannous sulfate solution and immediately attach the bottle to the aeration apparatus forming a closed system. Continue as described under Procedure (10.1).

Note 3 - Loss of mercury may occur at elevated temperatures.

However, with the stated amounts of acid the temperature rise is only about 13 C. (25-38 C) and no losses of mercury will occur (3).

10. Procedure

10.1 Transfer 100 ml or an aliquot diluted to 100 ml containing not more than 1.0 μ g of mercury to a reaction flask. Add 5 ml of sulfuric acid and 2.5 ml of nitric acid mixing after each addition (Note 3, 9.1). Add 15 ml of potassium permanganate solution to each sample bottle. Shake and add additional portions of potassium permanganate solution until the purple color persists for at least 15 minutes. Add 8 ml of potassium persulfate to each flask and heat for 2 hours in a water bath at 95 C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. Wait 30 seconds and add 5 ml of stannous sulfate to each flask individually and immediately attach it to the aeration apparatus. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously.

The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the by-pass valve and continue the aeration until the absorbance returns to its minimum value (Note 4). Close the by-pass valve, remove the stopper and frit from the reaction flask and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

Note 4 - Because of the toxic nature of mercury vapor, precaution must be take to avoid its inhalation. Therefore, a by-pass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

- (a) equal volumes of 0.1N KMnO_4 and 10% H_2SO_4
- (b) 0.25% iodine in 3% KI solution

11. Calculation

11.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

11.2 Calculate mercury concentration in sample by formula:

$$\mu\text{g Hg/liter} = \frac{\mu\text{g Hg}}{\text{in aliquot}} \times \frac{1000}{\text{volume of aliquot}}$$

12. Precision and Accuracy

12.1 A statement of precision and accuracy will be made available by the:

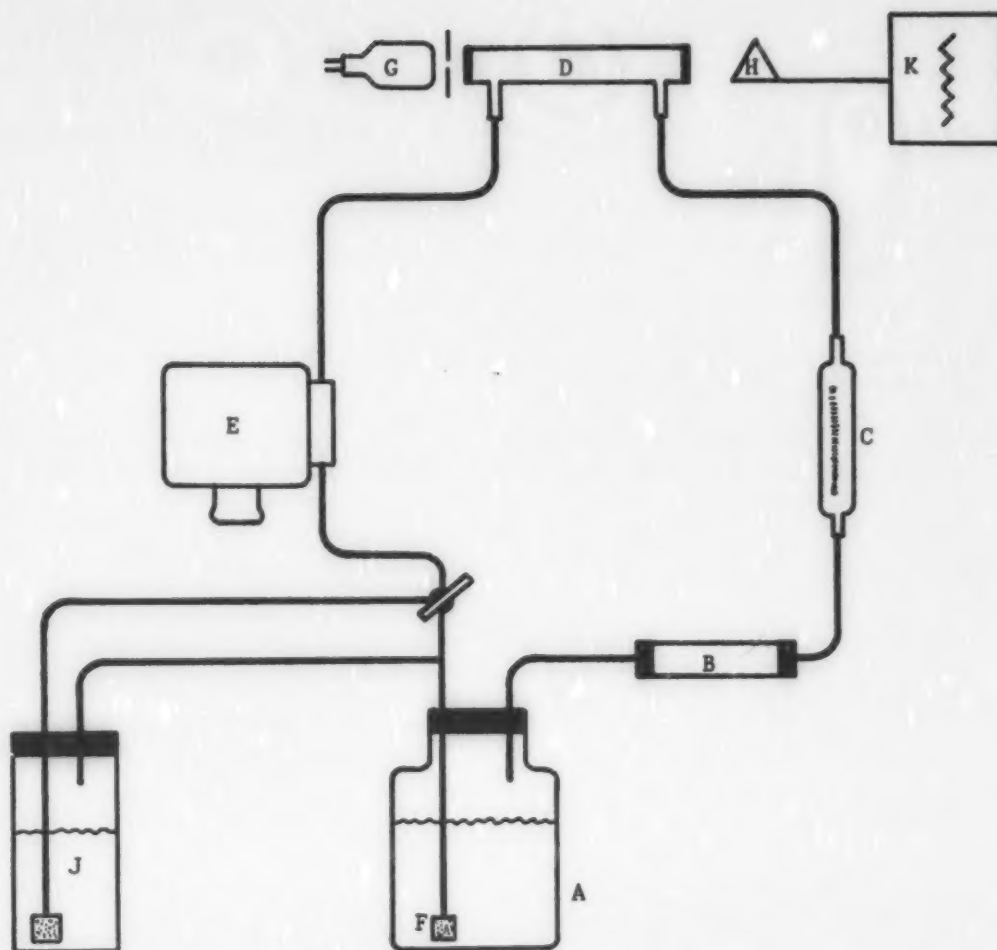
Quality Assurance Branch
Environmental Monitoring and Support Laboratory, EPA
Cincinnati, Ohio

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8. U.S. Environmental Protection Agency. Mercury Perservation Study, Region IV Surveillance and Analysis Division, Athens, Georgia. (Not Published)

SCHEMATIC ARRANGEMENT OF EQUIPMENT FOR MERCURY MEASUREMENT
by Cold Vapor AA Technique
Closed Recirculating System

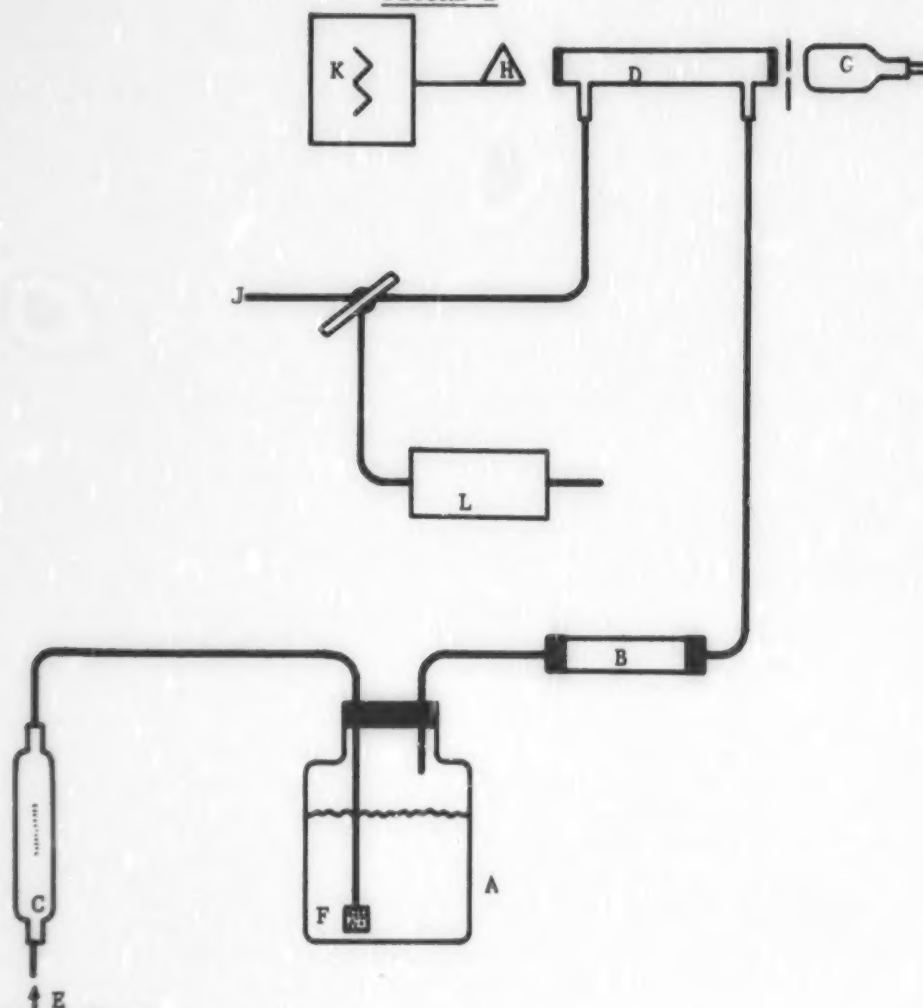
FIGURE 1



- A - Reaction Flask
- B - Drying Tube, filled with $MgClO_4$
- C - Rotameter, 1 liter of air/minute
- D - Absorption Cell with quartz windows
- E - Air Pump, 1 liter of air/minute
- F - Glass tube with fritted end
- G - Hollow cathode mercury lamp
- H - AA Detector
- J - Gas washing bottle containing 0.25% iodine in a 3% potassium iodine solution
- K - Recorder, any compatible model

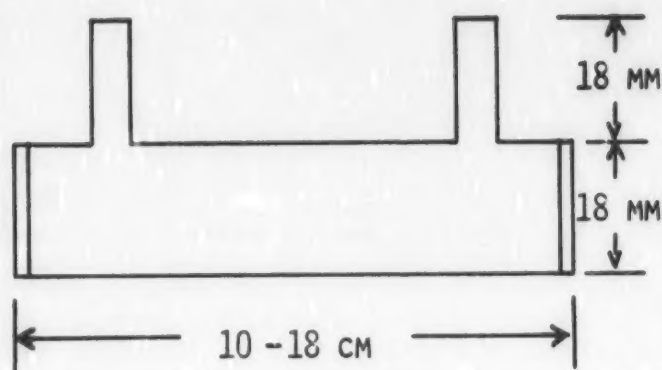
SCHEMATIC ARRANGEMENT OF EQUIPMENT FOR MERCURY MEASUREMENT
by Cold Vapor AA Technique
Open One-Pass System

FIGURE 2



- A - Reaction Flask
- B - Drying Tube, filled with $MgClO_4$
- C - Rotameter, 1 liter of air/minute
- D - Absorption Cell with quartz windows
- E - Compressed Air, 1 liter of air/minute
- F - Glass tube with fritted end
- G - Hollow cathode mercury lamp
- H - AA Detector
- J - Vent to hood
- K - Recorder, any compatible model
- L - To vacuum through gas washing bottle contain 0.25% iodine in a 3% potassium iodine solution

FIGURE 3



CELL FOR MERCURY MEASUREMENT
BY COLD VAPOR TECHNIQUE

The length and OD of the cell are not critical. The body of the cell may be of any tubular material but the end windows must be of quartz because of the need for UV transparency.

The length and diameter of the inlet and outlet tubes are not important, but the position of the side arms may be a factor in eliminating recorder noise. There is some evidence that displacement of the air inlet arm away from the end of the cell results in smoother readings. A mild pressure in the cell can be tolerated, but too much pressure may cause the glued-on end windows to pop off.

Cells of this type may be purchased from various supply houses.

APPENDIX

A1. Disposal of Mercury Containing Wastes

A1.1 Introduction

Mercury salts are components of the wastes from the following determinations:

- Chemical Oxygen Demand, D1252
- Ammonia in Water, D1426
- Chloride Ion in Industrial Water and Wastewater, D512
- Examination of Water Formed Deposits by Chemical Microscopy, D1245

Also, mercuric chloride is often used to preserve water samples for nitrogen and phosphorus analysis.

The safest way to retain mercury salts is as the sulfide at a high pH. Acidic solutions should be neutralized and combined with alkaline wastes and water samples containing mercury preservatives. To precipitate mercury, a convenient source of the sulfide ion is sodium thiosulfate. However, it should not be added to acidified wastes because of its rapid decomposition to elemental sulfur. The sulfur which precipitates increases the volume of sludge which must be processed and stored.

Mercury sulfide is insoluble and is stable to most reagents except aqua regia and bromine. Bacterial conversions to methyl mercury are prevented by maintaining the pH above 10.

A1.2 Procedure

Dilute all combined acidic wastes to about twice their original volume. Adjust the pH to greater than 7 by slowly adding sodium hydroxide solution (40-50 percent, w/v) with stirring. Combine this neutralized waste and any pooled alkaline wastes with stirring. At this point the combined wastes should have a pH of 10 or higher; if not, add sodium hydroxide until a pH of 10-11 has been obtained.

While the combined alkaline wastes are still warm, stir in small portions of sodium thiosulfate solution (40-50 percent, w/v) until no further precipitation seems to occur. Allow the precipitate to settle.

Draw off a few milliliters of clear supernatant, make sure the pH is still above 10, and then add an equal volume of sodium thiosulfate solution. If the supernatant still contains dissolved mercury, a precipitate will rapidly form, indicating that additional sodium thiosulfate must be added to the waste slurry.

After the precipitate has settled, decant or siphon off the clear tested supernatant and discard it. Wash the precipitate twice with water containing a trace of NaOH, allow to settle, and discard both of the clear washings. Dry the washed precipitate first in air, then in an oven at a temperature no higher than 110 C.

Store the dry solids until a sufficient quantity has accumulated to justify shipment to a commercial reprocessor: (Table 1).

Metallic mercury and waste organomercurials should be stored in suitable air tight containers until a commercial reprocessor can be contacted for specific shipping instructions: (Table 1).

TABLE 1

Reprocessors of Mercury (a)

Bethlehem Apparatus Co., Inc. Front and Depot Streets Hellertown, PA 18055 Phone: (215) 838-7034	M
Goldsmith Division, National Lead Co. 111 North Wabash Chicago, IL 60602 Phone: (312) 726-0232	M
Mallinckrodt Chemical Works 223 West Side Avenue Jersey City, NJ 07303 Phone: (201) 432-2500 (Mr. Frank L. Mackey, Western Branch Plant Manager)	MCO
Quicksilver Products, Inc. 350 Brannan Street San Francisco, CA 94107 Phone: (415) 781-1988 (Miss Grace Emmans, Owner and President)	MC
Sonoma Mines, Inc. P.O. Box 226 Guerneville, CA 95446 Phone: (707) 869-2013	C
Wood Ridge Chemical Corp. Park Place East Wood-Ridge, NJ 07075 Phone: (201) 939-4600 (Mr. E. L. Cadmus, Technical Director)	MC

M = Supplies flask for return of metallic mercury.

C = Will accept mercury sulfide for reprocessing.

O = Will accept certain organic mercury chemicals.

Note a - Special approval must always be obtained before shipment is made to a reprocessor.

GLOSSARY OF TERMS

The statistical measurements used in method study reports of the Environmental Monitoring and Support Laboratory-Cincinnati are defined as follows:

Accuracy as % Relative Error (Bias). The signed difference between mean value and the true value, expressed as a percent of the true value.

$$\text{R. E., \%} = \frac{\bar{X} - X_{\text{true}}}{X_{\text{true}}} \times 100$$

Confidence Limit (95%). The range of values within which a single analysis will be included, 95% of the time.

$$95\% \text{ C. L.} = \bar{X} \pm 1.96S$$

Mean Recovery. The arithmetic mean of reported values; the average.

$$\bar{X} = \frac{\sum X_i}{n}$$

Median. Middle value of all data ranked in ascending order. If there are two middle values, the mean of these values.

n. The number values (X_i) reported for a sample.

Range. The difference between the lowest and highest values reported for a sample.

Relative Deviation (Coefficient of Variation). The ratio of the standard deviation, S , of a set of numbers to their mean, $\bar{X}$, expressed as percent. It is an attempt to relate deviation (precision) of a set of data to the size of the numbers so that deviations at different mean values can be compared.

$$\text{R. D.} = 100 \frac{S}{\bar{X}}$$

Skewness (k). A pure number, positive or negative, which indicates the lack of symmetry in a distribution. For example, k is positive if the distribution tails to the right and negative if the distribution tails to the left.

$$k = \frac{\sum (X_i - \bar{X})^3}{nS^3}$$

Standard Deviation (S). The most widely used measure to describe the dispersion of a set of data. Normally, $\bar{X} \pm S$ will include 68 percent, and $\bar{X} \pm 2S$ will include about 95 percent of the data from a study.

$$S = \sqrt{\frac{\sum X_i^2 - \frac{(\sum X_i)^2}{n}}{n - 1}}$$

Standard Deviation: Single Analyst (S_r). A measure of dispersion for data from a single analyst. Calculated here using an equation developed by Youden based on his non-replicate study design.

$$S_r = \sqrt{\frac{\sum (D_i - \bar{D})^2}{2(n - 1)}}$$

t test. The difference between a single observation (X_n) and the estimated population mean ($\bar{X}$) expressed as a ratio over the estimated population standard deviation (S). The value obtained is compared with critical values from a table for the Student's *t* distribution. If the calculated *t* value exceeds the theoretical *t* value at a prescribed confidence level, the analyzed value is probably not from the same population as the rest of the data and can be rejected.

$$t = \frac{X_n - \bar{X}}{S}$$